Chapter 5

The role of Entropic and Enthalpic Forces on the macroscopic and microscopic phase transitions of Liquid Crystals:

This chapter describes the role of entropic and enthalpic forces mediated through organic non-polar/polar solvents and room temperature ionic liquids on the nature of the N-I phase transition of MBBA through calorimetric (macroscopic) studies and provides the molecular basis of such tunability through spectroscopic (microscopic) investigations.

Related publications


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5.1 Motivation

In this chapter, I shall discuss the changes in the macroscopic \( N-I \) phase transition of the \textit{nematic} liquid crystalline material in presence of entropic and enthalpic forces mediated through organic non-polar and polar solvents and room temperature ionic liquids. My motivation of this chapter is particularly to investigate whether in presence of entropic/enthalpic forces, the entropic activation barrier of \textit{nematic} liquid crystalline molecule changes its behaviour to fixed/ enthalpic activation barrier or preserves its entropic nature. I will provide the molecular basis of the tunability in the macroscopic phase behaviour of the \( N-I \) phase transition of \textit{nematic} liquid crystal in presence of these forces through molecular spectroscopy.

5.1 Motivation

As has been discussed in the introduction section, a mixture can be looked upon as a generalization of pure systems since it brings new concepts such as diffusion, coalescence, segregation, stability under segregation and the new quantities such as concentration, entropy of mixing, forces of adhesion as contrasted to forces of cohesion which result in the phase space of mixtures being richer than the pristine material and their structure and dynamics being much more complex and intriguing.

The system dynamics of mixtures evolve as an interplay between the competing forces of cohesion and adhesion. Some of these forces are entropic in origin and originate solely due to the entropy of mixing. On the other hand, enthalpic forces originate from specific interactions of the component molecules among their different kinds and among themselves. These forces are much more generalized in nature as they accompanied by the entropy of mixing and the introduction of extra degrees of freedom originating from the permanent dipole moment present in the system and they can be derived from the thermodynamic potentials. The effect of entropic/enthalpic forces on condensed matter systems is an important and challenging problem for the understanding of phase ordering or self assembly. Such forces can introduce either order...
or disorder which can dramatically alter the physical properties of the multicomponent, composite systems by coupling to the order parameter. It is also important to remember that no mixture is stable over its entire phase-space because the internal forces are always competing among themselves and given a suitable physical condition can start the process of segregation into its components through the formation of interfaces. Hence a mixture can always move to a non-equilibrium situation even under small external fields. Exploring a good physical system to study the effect of these forces thus offers a means to resolve problems in the understanding of complex interactions and non-equilibrium thermodynamics.

Liquid crystalline materials serve as attractive systems for complex interaction study as they exhibit a rich variety of complex phenomena because of a continuously variable orientational order parameter related to the molecular quadrupole moment. As the nematic ordering is pretty much sensitive to the external perturbations, phase behaviour of liquid crystals in this phase can be greatly influenced by entropic and enthalpic forces. In the previous chapter, I have shown that one such typical liquid crystalline molecule MBBA, which is in nematic phase at room temperature, possesses an entropic rather than enthalpic activation barrier, dependent on temperature, separating the nematic and isotropic phases and this leads to the convexity in the Arrhenius plots of the N-I transition. I have also investigated the molecular basis of such behaviour and come to the conclusion that conformational disorder due to large amplitude torsions leading to the non-coplanarity of the benzene rings in MBBA is responsible for such behaviour. Now the related fundamental question is can this activation barrier be tuned in presence of these forces and can interaction with the enthalpic forces lead to the change in the nature of the activation barrier to have a fixed (enthalpic) value? To answer such fundamental questions, first we need to introduce such forces in a simple and conceivable manner. The choice of material will be such that the mixtures can remain as a single phase in two component system
and sustainable in long term.

In this chapter I present a simple way to influence this activation barrier through mixing $MBBA$ in organic, low molecular weight, non-mesogenic solvents. Depending upon their molecular arrangement and inherent molecular interactions, different kinds of forces are present in the solvents. These forces can be broadly categorized into two distinct classes: (1) Entropic forces and (2) Enthalpic forces. Entropic forces are introduced to the liquid crystalline system through mixing with solvents such as non-polar solvents that have no specific long-range interaction with $MBBA$. The main effect of such solvents thus comes through the entropy of mixing. In such cases, solvent induced dilution weakens the intra-molecular forces between $MBBA$ molecules resulting in two main changes as has been pointed out by Iannacchione et al.\cite{125} namely (1) impurity effect and (2) viscoelastic softening. The impurity mechanism introduces concentration fluctuations (random local transition temperatures) and a generic truncation of the order parameter correlation length. Viscoelastic softening, on the other hand, can substantially change the order in the phase transition leading to an alternation of the physical properties. Enthalpic solvents such as organic polar solvents, on the other hand, provide enthalpic forces which appear due to the permanent dipole moment present in these solvents. Thus enthalpic solvents provide mixing entropy as well as extra new degrees of freedom. The mixing entropy in these solvents plays an subservient role compared to the effect produced by the dipolar interaction. Hence, apart from the above mentioned effect, extra features may be added to the phase transition of nematic liquid crystal in presence of enthalpic solvents. Each of these classes of solvents interact in an unique manner with the liquid crystalline system and thus a contrast in the phase transition behaviour is observed amongst them that can be used to understand their distinct effects.

Over the last few years a renewed attention has been drawn to mixtures of liquid crystals and nonmesogenic, low-molecular weight solvents\cite{126–128}. The focus of
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Coulomb forces, i.e. free ions. The only available pristine sources of free ions that remain stable under ambient conditions are room temperature ionic liquids (RTILs). The properties of the RTILs are known to be mainly governed by the Coulomb interactions between the free ions. Other interactions such as hydrogen bonding, van der Waals and other dispersive forces are also present but they play relatively minor roles. The intriguing features of the RTILs, their different interactions and the factors which give the stability of the RTILs at room temperature will be discussed briefly in the forthcoming section. As the strength of Coulombic interaction between the component ions is one order higher than the dipolar strength in the polar solvents, the former can be considered as strong enthalpic solvents and introduction of RTILs can cause dramatic changes in the phase diagram of the liquid crystalline material. To my knowledge phase transition of liquid crystal in presence of RTIL has not been addressed before and in this thesis I will discuss the phase transition of such mixtures. As RTILs are constituted of large cations (such as imidazolium) and considerably large anions (inorganic), the screening of the intermolecular potential of is expected to occur at much low concentration of RTIL compared to the polar organic solvents. Hence the motivation of my present study is as follows:

- To investigate the phase transition of MBBA in presence of entropic and enthalpic forces mediated through organic non-polar and polar solvents as well as room temperature ionic liquids. More specifically I want to distinguish the screening mechanisms among these solvents. For this, I have performed detailed differential scanning calorimetry measurements of the mixtures of MBBA with hexane (non-polar), methanol (polar) and 1-ethyl-3-methylimidazolium tetra-chloroferrate (RTIL) around the vicinity of the N-I transition at different molar ratios and a particular (fixed) heating rate.

- To investigate whether in presence of these solvents or forces, the non-Arrhenius feature of MBBA is still retained or the inter-molecular interaction causes a...
change in the molecular dynamics to follow Arrhenius like behaviour. In order to examine this, I have performed detailed rate dependent differential scanning calorimetry for a fixed mol% of these solvents at various heating rates.

- To understand the molecular basis of these solvent induced changes. For this, I have performed detailed FTIR and UV-Visible spectroscopy of these mixtures at similar concentrations of hexane, methanol and RTILs as in the calorimetric studies.

## 5.2 Room Temperature Ionic Liquids

In this section I will discuss the properties and a brief history of room temperature ionic liquids. Ionic liquids are salts which consists entirely of ions where the ions are very poorly coordinated[134]. This results in these solvents being in the liquid state below 100°C[135, 136] or even at room temperature which gives them the name room temperature ionic liquids (RTILs). RTILs are made up of bulky cations and considerably large anions[137], at least one of them have delocalized charge distribution[138] and one component is organic, whose internal degrees of freedom prevent the formation of a stable crystal lattice. RTILs are currently the focus of extensive investigation primarily because they hold promise as environmentally-friendly media[139] and could be a possible alternative to the volatile organic chemicals that are used as solvents, due to their negligible vapor pressure. Wide liquidus, thermal stability, high ionic conductivity, miscibility with other solvents, and recyclable nature are some other properties[140, 141] that make these liquids suitable as solvents for various applications. These ionic liquids are often termed as designer solvents[142]since an appropriate combination of the cationic and anionic constituents may provide an RTIL with desired properties[143]. The increasing usage of these ionic liquids as media for organic synthesis [144], liquid-liquid extraction[145],
electrochemical studies[146], mass spectrometry[147], solar cells[148], synthesis of nanoparticles[149, 150], gas sensor[151], catalysis, material sciences, chemical engineering and energy related applications such as batteries[152], optical sensors[153], fuel cells[154], photovoltaics[155], supercapacitors[156] etc is clearly evident from the literature.

The history of ionic liquids (and the closely related molten salts) has a rather ill-defined beginning, in general they are dated back to 1914, to the work of Walden on the use of alkylammonium nitrates[157]. The next burst of interest occurred with the discovery of chloroaluminates formed by combining quaternary heterocyclic cations with aluminium chloride. These materials exhibited a great deal of potential for use in a variety of areas, but all suffered from extreme sensitivity to moisture. A major step forward was made by Wilkes in the early 1990s, with the report of moisture stable ionic liquids created by replacing the aluminum chloride with other anions, such as tetrafluoroborate or hexafluorophosphate. Since that seminal report by Wilkes and co-workers[158], the family of RTILs has seen explosive growth. Starting with imidazolium cations, the cationic component has been varied to include pyridinium, ammonium, phosphonium, thiazolium, and triazolium species. In general, these cations have been combined with weakly coordinating anions, although not all weakly coordinating anions result in RTILs (for example, the very weakly coordinating polyhedral borane anions of Reed afford salts with melting points between 45°C and 156°C for a series of imidazolium cations). Common examples of RTILs contain tetrafluoroborate, hexafluorophosphate, triflate, triflimide, and dicyanamide. The first two have been explored the most, and must be treated with the greatest caution as they are fairly readily hydrolyzed to boric acid and phosphate respectively. Indeed, various phosphate and phosphinate anions have been employed to some advantage in RTILs. The list of possible anionic components continues to grow at a rapid rate.

Room temperature magnetic ionic liquids (RTMILs) are the latest development of
RTILs, promising new materials that will allow further features to be added to the typical properties of ILs, such as magnetic, photophysical/optical[159], or electrochromic behavior[160], all of which are due to the incorporated metal. They were discovered in 2005 by Hayashi et al.[161] in studies carried out on 1-butyl-3-methylimidazolium tetrachloroferrate \([\text{Bmim}]^+ [\text{FeCl}_4]^−\), which has a paramagnetic behavior with an effective moment of 5.8 \(\mu_B\). Typically, MILs are composed of metal containing anions, such as iron, cobalt[162], manganese[163], copper[164], etc. Nowadays, the development of these MILs has led to different rare-earth[165] (neodymium[166], gadolinium, dysprosium[167]), chiral amionacids (MCILs)[168], or bimagnetic ions[169] being combined. Therefore, the synthesis, study, and application of these new materials are growing exponentially[170]. As regards to the technological applications of MILs, due to their high magnetic response to external magnetic fields, they can be used for the transport and separation of materials[171, 172], as an absorbent for benzene emissions[173], in catalysis[174] and sulphide (SO\(_x\)) extraction in gasoline[175], as a greenhouse gas (CO\(_2\) and SO\(_2\)) absorbent[176], as new magnetic materials[177], or in biotechnology[178].

In ionic liquids, the major interaction that gives the stability of these structure is the Coulombic interaction (mutual electrostatic attraction or repulsion of the free ions) between the counter-ions which makes them miscible with substances having very wide range of polarities and enable them to dissolve organic and inorganic substances. Naturally, electrostatic interactions are a major source of cohesion. In addition to this, hydrogen bonding, dipole-dipole and van der Waals interactions are present in RTILs. Hydrogen bonding in RTILs is thought to exist between an oxygen or halide atom on the anion and the hydrogen atoms on the imidazolium or pyridinium ring of the cation.
5.3 Effect of Organic Solvents on the phase transition of Nematic Liquid Crystal:

In order to investigate the effect of entropic and enthalpic forces mediated through organic solvents on the phase transition of MBBA, I chose non-polar n-Hexane and polar methanol as model solvents for the carriers of entropic and enthalpic forces.

For sample preparation, a specified amount of MBBA was transferred to a vial and relatively large amount of solvents were added and thoroughly ultrasonicated to a uniform solution. The mass of the solution was constantly monitored. The organic solvent was then slowly allowed to evaporate until the desired mass of mixture was attained. At this point, the vial was properly sealed and special precautions were taken to ensure that desired amount of sample remained sealed within the vial.

The phase transition of the mixtures were thoroughly investigated through differential scanning calorimetry. Measurements were performed at commonly used ramp rate of 10 K/min when phase transition of MBBA were investigated as a function of solvent concentration. Also, a heating rate dependent DSC study were performed using multiple heating rates keeping the solvent concentration fixed. I provide the experimental results separately for methanol and hexane in this section.

First, I focus on the modulation of the phase transition of MBBA in presence of hexane. A detailed DSC study on the mixtures of MBBA with 5, 10, 15, 20, 25 and 30 mol % of hexane concentration was performed around the vicinity of the N-I phase transition of MBBA during cooling scan and the variation of the phase transition temperatures with hexane concentrations are shown in Figure 5.1(a). The thermograms were taken after fast quenching of the mixtures by liquid nitrogen from room temperature (298 K) to 173 K, equilibrated for several minutes and then reheated to 323 K at faster heating rate of 50 K/min. This procedure removes the possibility of any phase separation within the mixture. This was verified (Figure 5.1(b)) in both
heating (inset) and cooling (main) scans through multiple thermal cycling of the mixture with the highest mole percentage of hexane (30 mol%) whereby the mixture was found to be completely stable even after the third cycle in each case.

The DSC signals were monitored during a cooling scan at 10 K/min from 323 K. A continuous decrease in the transition temperature is observed with hexane concentration as indicated in Figure 5.1(c). Introduction of hexane causes increase in the mean inter-molecular separation ($r$) of MBBA and as a consequence, the interaction potential between the MBBA molecules decreases leading to the decrease in the transition temperature. The most effective way to understand this effect is to measure the inter-molecular potential of MBBA and plot it as a function of $r$. A decrease in the inter-molecular potential of MBBA with $r$ is shown in Figure 5.1(c), where the right ordinate and upper abscissa denote the inter-molecular potential and $r$, respectively. The figure indicates a linear decrease in the transition temperature with hexane concentration, while a slight non-linearity is observed in the interaction potential with $r$. To bring this out, the variation of the interaction potential with $r$ is fit with both linear and parabolic functions, where the parabolic function is seen to give a much better fit.

The decrease in the interaction potential and thus the transition temperature of MBBA is attributed to the entropic screening by the hexane molecules. Since screening presumably plays an important role, I specifically wanted to measure this effect as a function of the mean distance between the hexane molecules ($\bar{l}$). I assume that hexane molecules are uniformly distributed throughout the mixture. The value of $\bar{l}$ may be estimated from the specific volume (volume per molecule) of the MBBA and that of hexane. For hexane and MBBA, the specific volume was estimated to be $v_{\text{Hexane}} = 218.17 \text{Å}^3$ and $v_{\text{MBBA}} = 431.64 \text{Å}^3$ respectively. The boundary values in the relation between $v_{\text{mix}}$ (specific volume of the average molecule of the mixture), $v_{\text{hexane}}$, $v_{\text{MBBA}}$ and $x_{\text{hexane}}$ (mole fraction of hexane) are goes as $v_{\text{mix}} = v_{\text{MBBA}}$ when
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For \( x_{\text{Hexane}} = 0 \) and \( v_{\text{mix}} = v_{\text{hexane}} \) when \( x_{\text{Hexane}} = 1 \). The relation as obtained from the fit in Figure 5.1 (d) is

\[
v_{\text{mix}}(x_{\text{hex}}) = -213.46x_{\text{hex}} + 431.63 \quad (5.1)
\]

If I consider the hexane molecules to be uniformly distributed with each center in a spherical unit cell

\[
v_{\text{mix}} = x_{\text{hex}}(\pi l^3/6) \quad (5.2)
\]

This volume in the unit cell times the total number of hexane molecules gives the total sample volume divided by the total number of molecules. From these definitions of \( v_{\text{mix}} \), I obtain

\[
\bar{l} = [6\pi (v_{\text{mix}}(x_{\text{hex}}))/(x_{\text{hex}})]^{1/3} \quad (5.3)
\]

This dependence of mean separation between the hexane molecules (\( \bar{l} \)) is shown as a function of hexane mole fraction in inset Figure 5.1(d), which indicates decrease in the hexane molecular separation with increasing hexane concentration. For \( \bar{l} \) smaller than the length scale for the LC interaction, the screening effect on the LC molecular interaction should be dominant. The average molecular length of MBBA is approximately 18 Å. Hence, for \( l \leq 18\text{Å} \), the hexane interaction with MBBA will be dominant. Inset Figure 5.1(d) clearly indicates the threshold mole fraction of hexane for this comparable value is \( \simeq 0.10-0.15 \), below which a weaker screening of the LC molecules by the hexane molecules is expected.

The above discussion indicates that the introduction of hexane causes decrease in the inter-molecular potential of MBBA by creating separation between MBBA molecules. I explain this situation with the aid of the ‘depletion force’ model proposed by Asakura and Oosawa (AO) model[123]. This model is particularly useful in describing mixtures that are stable in bulk but without any direct interaction between solute and solvent particles. It has been widely used to explain situations where a mi-
crophase segregation takes place inspite of stability in the bulk. As MBBA has rigid rod molecules relative to the hexane molecule, the region between MBBA molecules is eventually crowded by hexane molecules as they ‘wiggle’ in between the rod-like MBBA molecules. The AO model describes a situation when two solid plates are immersed in a solution of spherical macromolecules. If ‘a’ is the distance between these two plates, ‘d’ the diameter of the solvent molecule and $a < d$, none of the solvent molecules can enter between the plates. Then, the region between the plates will be depleted of molecules, the solvent outside this plate is little affected by them and a force equivalent to the osmotic pressure (the depletion force) acts inward on each plate. Here, on the other hand, the interacting hexane molecules exert force on MBBA molecules which pushes them apart and creates a separation between them. In this situation $a > d$ when hexane molecules are allowed to enter the region containing MBBA, and this goes on until $a >> d$, the depletion region is completely gone and the correlation between successive MBBA molecules is considerably reduced. The situation can be thought of as the static parallel plates in a highly viscous medium with constant viscous drag where the interaction potential between MBBA molecules decreases as

$$V(r) = V_0 - \kappa r$$

, where $\kappa$ is a constant viscosity term. In this model the MBBA-hexane adhesion is dominant and the interaction potential between MBBA molecules and phase transition temperature decreases linearly with increasing intermolecular separation $r$. However, cohesion between MBBA molecules plays a restorative role giving rise to a natural frequency with which the MBBA molecules can oscillate. Hence, it is more physically sensible to consider the ‘plates’ of MBBA molecules (the effective area occupied by the benzene rings) to oscillate with an angular frequency $\omega$ in a high viscous medium. In this model, the interaction potential of MBBA then decreases
5.3. Effect of Organic Solvents on the phase transition of *Nematic* Liquid Crystal:

according to the relation

\[ V(r) = V_0 - \kappa r + \omega r^2 \]

In Figure 5.1(c), both the decrease in the *N-I* phase transition temperature and the interaction potential of *MBBA* with increasing hexane mole fraction are fitted accordingly to the static and dynamic models and the oscillatory model gives a better fit.

In the case of polar solvent, methanol, the scenario is quite different. Methanol, having permanent dipole moment, has the tendency to interact with the dipolar imine bond of *MBBA*, while it does not interact with the out-of-plane vibration of the benzene rings. The dipole moments of methanol try to align themselves parallel to the direction of the local electric field created by the imine bond keeping the distance between two *MBBA* molecules intact. In other words, methanol molecules try to create solvation spheres around *MBBA* molecules and as a consequence they screen the inter-molecular potential of *MBBA* resulting in a decrease in the phase transition temperature of *MBBA*. However, as the number of methanol molecules increases, they will also start to self-screen themselves which results in a saturation in the screening and hence saturation in the phase transition temperature as shown in Figure 5.1(e).

In Figure 5.1(f), multiple thermal cycles for *MBBA-methanol* mixtures for the highest value of methanol concentration (25 mol%) is shown which indicates stable and well reproducible results for each cycle with almost the same transitional temperature and enthalpy of transition. The variation of *T_C* with methanol concentration and that of the intermolecular interaction of *MBBA* with the intermolecular separation are shown in Figure 5.1(g). The figure indicates a small variation in *T_C* from 5 to 10 mol% of methanol concentration indicating the initial phase of screening. An abrupt jump in *T_C* from 10 to 15 mol% of methanol is observed which indicates completion of screening around this concentration. Beyond that, a saturation in the *T_C* is observed which corresponds to the self screening phenomena. *T_C* is also found
to decay sigmoidally with methanol concentration which explains well this screening and self screening phenomena.

The change in enthalpy associated with the $N$-$I$ transition of $MBBA$ are shown as a function of hexane and methanol concentrations in Figure 5.1(h). The value of the transitional enthalpy for neat $MBBA$ is also shown in the same figure which again exhibits the screening of the inter-molecular potential of $MBBA$ in presence of these solvents. Here I also observe a continuous decay of transitional enthalpy for hexane following a parabolic behaviour and a saturation behaviour for methanol after an initial decay phase following a sigmoidal behaviour.

Plausible schematics for the screening behaviour in presence of hexane and methanol are depicted in Figure 5.2(a) and 5.2(b).

5.3.1 Rate dependent Differential Scanning Calorimetry study

The effect of entropic vs enthalpic forces on the phase transition of $MBBA$ was further investigated through the Arrhenius/non-Arrhenius dependence of the $T_C$ of $MBBA$ in presence of hexane and methanol. In Chapter 4, I have shown that the $N$-$I$ phase transition of pristine $MBBA$ exhibits non-Arrhenius behaviour through its dependence on the configurational/conformational entropy and this configurational entropy arises due to the torsional motion about the C-C bond that makes the benzene rings non-coplanar leading to change in the imine stretch and the out-of-plane distortion vibrations of the benzene rings, as confirmed by detail calorimetric and spectroscopic investigations. I have also shown that $N$-$I$ transition is indeed a non-equilibrium phase transition as it depends on the thermal history and time scale of observation[179]. In presence of entropic solvents like hexane the activation barrier of the $N$-$I$ transition of $MBBA$ is expected to retain its non-Arrhenius behaviour since there is no direct energetic interaction between $MBBA$ and hexane and the screening is facilitated only through the short-range repulsion between the solute and solvent.
5.3. Effect of Organic Solvents on the phase transition of Nematic Liquid Crystal:

![Graphs showing the effect of organic solvents on the phase transition of nematic liquid crystals.](image)

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5.3. Effect of Organic Solvents on the phase transition of *Nematic* Liquid Crystal:

![Graph](image)

Figure 5.1: (a) Excess Specific Heat capacity (J/gK) vs Temperature (K) plot for *MBBA* for various hexane concentrations (C\text{Hex}) indicated in the inset during cooling scan. (b) Multiple thermal cycles for *MBBA* in presence of 30 mol% hexane concentration. The cooling cycles are represented by solid line (first cycle), dashes (second cycle) and dots (third cycle) respectively. Inset: The same for the heating cycles with the same usual meaning of the color symbols. For the sake of visual clarity, the $\delta C_P$ axis is inverted to the positive value. (c) Variation of isotropization temperature of *MBBA* with hexane concentration (left ordinate, lower abscissa) fit with linear (dot) function. Variation of the interaction potential with the inter-molecular separation between the *MBBA* molecules (right ordinate, upper abscissa) along with linear (solid line) and parabolic (dotted line) fit. (d) Plot of specific volume (volume per particle) of the *MBBA*-Hexane mixture vs hexane mole fraction ($x_{\text{Hex}}$) where the circles represent the calculated specific volume along with a linear fit (solid line). Inset: calculated mean distance between the hexane molecules ($\bar{l}$) vs the hexane mole fraction plot (triangles) along with an exponential fit (solid line). (e) DSC thermograms for *MBBA*-methanol mixtures at various methanol concentrations (C\text{MeOH}) (indicated in the inset) around the isotropization temperature of the mixture. (f) Multiple thermal cycles for *MBBA* in presence of 30 mol% methanol concentration. The cooling cycles are represented by solid line (first cycle), dashes (second cycle) and dots (third cycle) respectively. (g) Variation of the isotropization temperature with methanol concentration (squares) (left ordinate, lower abscissa) along with a logistic function (blue line) and interaction potential vs inter-molecular separation between the *MBBA* molecules (circles) (right ordinate, upper abscissa) fitted with a logistic function (red line). (h) Variation of transitional enthalpy ($\Delta H$) with hexane (circles) and methanol (triangles) concentration along with logistic (red line) and parabolic (blue line) fit respectively. The $\Delta H$ value for neat *MBBA* is shown as a separate point in the plot.
molecules. On the other hand, in methanol the enthalpic force comes from the permanent dipole moment present in the molecules that can interact with the dipole moment of the imine bond in MBBA and this may take the non-Arrhenius behaviour to Arrhenius behaviour.

To test all these possibilities, I have employed a detailed heating rate dependent differential scanning calorimetry study on the mixtures of MBBA with 5 mol% of hexane and with 5 mol% of methanol concentration around the vicinity of the N-I phase transition of MBBA. In Figures 5.3(a) and 5.3(b), the representative thermograms during heating scans at various heating rates of 2, 5, 8, 10 and 12 K/min are shown for hexane and methanol respectively. The peak temperatures in both these cases were taken as the representative transition temperature and it was observed that with increasing heating rate, transition temperatures shift towards higher values indicating the kinetic nature of the phase transition of the mixtures. In Figure 5.3(c), Arrhenius plots are shown for both these mixtures, where the lower and upper abscissae represent the temperature scales for hexane and methanol respectively. The representative data points for hexane show pronounced non-Arrhenius behaviour and can be best fit by a logistic function. In Figure 5.3(d), Arrhenius plots for neat MBBA is shown where the data points are best fit by a monomolecular growth function as described in the previous chapter. The curvature of the Arrhenius plots for MBBA and its mixture with hexane indicates that the non-Arrhenius behaviour of MBBA is not only retained but also gets enhanced in presence of hexane. For methanol, on the other hand, the data points show linear dependence on the heating rate exhibiting the Arrhenius behaviour. This indicates that the enthalpic interaction with methanol takes the system to follow non-Arrhenius to Arrhenius behaviour.

From these results it is clear that while entropic screening preserves the non-Arrhenius feature of the N-I transition in MBBA, enthalpic screening destroys this feature and makes the system to follow Arrhenius behaviour.
5.3. Effect of Organic Solvents on the phase transition of Nematic Liquid Crystal:

Figure 5.2: Schematic representation of (a) entropic and (b) enthalpic screening. For the entropic screening model (as shown in (a)), the circles are 2-D projection of ‘gyration spheres’, i.e. the spheres produced by the random rotation of the chains or the molecular dipoles while in (b), the spheres are the permanent dipole moment of the methanol solvent itself.

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Figure 5.3: (a) Heating rate dependent DSC study for the mixtures of MBBA with 5 mol% hexane concentration at 2 (line), 5 (dash), 8 (dot), 10 (dash dot) and 12 (dash dot dot) K/min respectively. (b) The same for 5 mol% methanol concentration at 2 (line), 5 (dash), 8 (dot), 10 (dash dot dash) and 12 (dash dot dot) K/min respectively. (c) Natural logarithm of ramp rate (ln β) vs inverse of temperature (1000/T (K^-1)) plots for MBBA-hexane (lower abscissa, circles) and MBBA-methanol (upper abscissa, triangles) mixtures. The data points for MBBA-methanol mixture are fitted with a straight line (red line) showing Arrhenius behaviour and that of the MBBA-hexane mixture with Sigmoidal function (blue line) showing non-Arrhenius feature. (d) Natural logarithm of ramp rate (ln β) vs inverse of temperature (1000/T (K^-1)) plot for pristine MBBA showing non-Arrhenius behaviour. The data points are fitted by a monomolecular growth model.
5.4 Molecular Basis of the Arrhenius-non Arrhenius behaviour:

These results from differential scanning calorimetry study indicating a change over from non-Arrhenius to Arrhenius behaviour on changing from an entropic or non-polar to an enthalpic or polar solvent and the indication of distinct screening mechanisms suggest a deep connection with the interactions in the molecular level as well as the molecular conformations. I have performed detailed FTIR and UV-Vis spectroscopy to understand the possible role of these solvents on the molecular interactions of MBBA. FTIR spectroscopy for these mixtures was performed using Perkin Elmer Spectrum 400 spectrophotometer. To avoid any volatility of the organic solvents from the mixture, the samples were filled in a standard liquid cell procured from Specac as described in Chapter 2. After each measurement, the sample cell was thoroughly rinsed with acetone and ethanol and then properly dried. The FTIR measurements were performed around the vicinity of imine (C=N) stretch (1600-1650 cm\(^{-1}\)) and out-of-plane distortion vibrations of the benzene rings (800-900 cm\(^{-1}\)) of MBBA. For each measurement, 500 scans were performed with proper background correction. UV-Visible (UVVis) spectroscopy was performed using JASCO V650 (Jasco, Japan) spectrophotometer which is equipped with a peltier temperature controller. Temperature control was done using ethylene glycol-water mixture. Standard quartz cuvette of dimension 4.5\(mm\) \(\times\) 12.5\(mm\) \(\times\) 12.5\(mm\) and path length of 10 mm was used for this purpose. After each measurement, the solutions were thrown out from the cuvette, properly rinsed with mili-Q water followed by acetone and ethanol treatments, and finally dried carefully. After that, a spectrum of cuvette filled with pure solvent was taken to ensure no traces from the previous experiment present in the signal.

FTIR spectroscopy deals with the different vibrational modes such as stretching, bending, wagging etc associated with the molecule and it is very sensitive to any
environmental changes and thus very useful to study different molecular interactions in variety of mixtures. The molecular motion and thus the properties of MBBA are solely determined by the stretch vibration of the imine (-C=N) bond in conjunction with the out-of-plane distortion vibration of the benzene rings attached to the imine bond. The well defined peak at 1625 cm\(^{-1}\) corresponds to the imine stretch vibration and the peaks at 836 and 888 cm\(^{-1}\) are attributed to the out-of-plane distortion vibrations of two differently substituted benzene rings of MBBA. These bands thus are the bands to investigate solvent induced change in the molecular behaviour of MBBA.

Measurements on MBBA-hexane and MBBA-methanol mixtures were done under ambient conditions with similar concentrations of solvents taken as in the calorimetric measurements. In Figure 5.4(a), the FTIR spectrum of MBBA with varying hexane concentrations of 5-30 mol% around the vicinity of imine stretch is shown. The plot of integrated IR intensity with hexane concentration is shown inset the same figure. A parabolic decrease in the imine stretch intensity with hexane concentration similar to that observed in \(T_C\) vs hexane concentration plot in DSC is noticed. These features indicate loss of correlation between the imine stretch of MBBA molecules, which is consistent with our proposed entropic screening model. I expect a linear decrease in the imine stretch intensity with hexane concentration. Small deviation from linearity appears in the data (Inset Figure 5.4(a)) probably because of the residual long range dipolar interaction present among the MBBA molecules due to the imine bond. In contrast, due to the absence of any long range interactions in the benzene rings, the molecular motions of the benzene rings become uncorrelated and the intensity decreases linearly with increasing hexane concentration as shown inset Figure 5.4(b) and fits almost exactly our proposed model for entropic screening.

In case of methanol, saturation in the imine stretch intensity with methanol concentration is observed after quick decay from 5 to 8 mol% exhibiting 'screening' and 'self-screening' phenomena (Figure 5.4(c)). This saturation is similar to the previ-
ously observed saturation behaviour of $T_C$ and $\Delta H$ with methanol concentration from calorimetry study. This indicates that owing to the polar nature of methanol, it can quickly build solvation spheres around MBBA resulting in the screening effect. In latter stages, methanol molecules self-screen so that no new methanol molecules interact with MBBA leading to saturation in the imine intensity as shown inset Figure 5.4 (c). Thus, the screening and self-screening phenomena are well explained in macroscopic as well as in the microscopic scale, and are consistent with our proposed enthalpic screening model. However, due to the polar nature of methanol, it has almost no interaction with the benzene rings that have no permanent dipole moment. Thus, methanol has no net effect on the out-of-plane distortion vibrations of the benzene rings, resulting in no net variation in intensity as shown inset Figure 5.4 (d).

Temperature controlled UV-Vis spectroscopy allows us to probe distinct molecular interactions between MBBA and these solvents in terms of different functional dependences of the intensity of the electronic transition of MBBA on temperature. The change in the spectral intensity of any electronic band with temperature obeys an exponential relation

$$I = I_0 \exp\left(-\frac{E_{a}^M}{kT}\right) \quad (5.4)$$

where $I$ is the intensity of any spectral band and $E_{a}^M$ is the activation barrier of the particular excitation for a singlet molecule.

I have employed a detailed UV-Vis spectroscopy of MBBA in presence of methanol and hexane in UV range 250-400 nm. Pristine MBBA exhibits high absorption in UV region and due to this the spectrum is difficult to acquire as it quickly saturates the signal even at low gain, hampering resolution very seriously. Hence, significant dilution by solvents is necessary to capture the spectrum. The concentrations of MBBA in both methanol and hexane are adjusted to milimolar ($5 \times 10^{-3}$ M) . Between 250-400 nm, pristine MBBA exhibits double humped absorption peaks at around 280 (peak I) and 320 (peak II) nm. With increasing solvent polarity, peak I
Figure 5.4: (a) Fourier Transform Infrared (FTIR) spectra of MBBA around the imine stretch vibration (1615-1640 cm$^{-1}$) in presence of 5-30 mol% of hexane concentration indicated in the left inset. Right Inset: variation of integrated IR intensity with hexane concentrations (circles) along with parabolic fit (red line). (b) The same for the out-of-plane distortion vibrations of the benzene rings (820-900 cm$^{-1}$) with the color symbols have the same meaning. Inset: The variation of integrated IR intensity vs hexane concentrations (circles) along with a linear fit (red line). (c) and (d) represents FTIR spectra of MBBA for the imine stretch and out-of-plane distortions respectively in presence of 5-30 mol% of methanol as indicated in the insets of these figures. Inset (Figure 5.4 (c)) represents the variation of imine stretch intensity with methanol concentrations (circles) along with a Slogistic fit (red line) and Inset (Figure 5.4 (d)) represents the same for out-of-plane distortion vibrations of the benzene rings. The red dotted line guide to the eye indicating no net variation in intensity. In all of the above figures the mole concentrations of hexane and methanol are represented by $C_{Hex}$ and $C_{MeOH}$ and the integrated IR intensity of the bands are represented by $I_{Hex}$ and $I_{MeOH}$ respectively.
5.5. Phase Transition of Nematic Liquid Crystal in presence of a Room Temperature Ionic Liquid:

shifts towards higher wavelength, while peak II towards lower. So, the appearance of peak I is attributed to the $\pi \rightarrow \pi^*$ transition of the electrons in the imine (-C=N) bond and peak II is due to the $n \rightarrow \pi^*$ transition. In Figures 5.5(a) and 5.5(b), the absorption spectra for MBBA in hexane and methanol as a function of temperature are shown. In both the solvents, I observe a decrease in the spectral intensity for both these bands from room temperature (298 K) to well into the isotropic phase ($\sim 318$ K) of MBBA. I focus my attention only on the solvent induced change in the spectral intensity of peak I as a function of temperature. Peak I (boxed region in Figure 5.5(a)) in MBBA-hexane mixture shows blue shift with increasing temperature accompanied with a large fall in intensity, while MBBA-methanol mixture indicates only a small change in intensity with no positional shift (Figure 5.5(b)). Insets both these figures, the spectral intensities (I) were plotted against inverse of temperature ($1/T$). In hexane, the intensity is found to follow exponential behaviour, while it shows linear dependence in methanol. This indicates that for MBBA, hexane acts as a non-interacting medium, while enthalpic interaction with methanol controls the behaviour of the corresponding mixtures.

5.5 Phase Transition of Nematic Liquid Crystal in presence of a Room Temperature Ionic Liquid:

Having confirmed the distinct roles of entropic and enthalpic forces mediated by organic solvents, I proceed to check the role of Room Temperature Ionic Liquids on the phase transition of MBBA. I have taken similar experimental approaches for this, i.e., investigating the bulk behaviour of N-J phase transition of MBBA in presence of RTILs through calorimetry and exploring the molecular basis of such transitional behaviour through FTIR spectroscopy. Since RTILs are charge driven systems, they have a tendency to phase separate from the liquid crystalline material. Hence low
5.5. Phase Transition of *Nematic* Liquid Crystal in presence of a Room Temperature Ionic Liquid:

In my experiment I have used the Fe based room temperature paramagnetic ionic liquid 1-ethyl-3-methylimidazolium tetrachloroferrate ([Emim]⁺[FeCl₄]⁻) (EMIF) as a model compound for investigating its interaction with MBBA. Upon resonant excitation to a charge transfer state, this ionic liquid exhibits an unusually long-lived macroscopic polarization state which is referred to as a non-equilibrium quasi-stationary state. It is interesting to note that, this type of state is not present in the related 1-ethyl-3-methylimidazolium tetrachlorogallate (EMIG)[180]. As MBBA exhibits non-equilibrium characteristics in its N-I transition, it is therefore interesting to investigate whether the long range interactions between MBBA and EMIF (i) is predominantly charge-quadrupolar or dipolar-quadrupolar in nature and (ii) is sufficient to destroy the non-Arrhenius behaviour of the MBBA N-I transition. Besides concentration of RTIL in the mixture is preferable. Besides, special experimental precautions are also needed in order to achieve and maintain of the mixture in single phase.

Figure 5.5: (a) UV-Visible spectra of MBBA at $5 \times 10^{-3}$ M concentration in hexane from room temperature (298 K) to 323 K. Inset: Plot of intensity vs inverse of temperature (1000/T) (K⁻¹) along with an exponential fit (red line) for peak I indicated by a square. (b) the same for MBBA-methanol mixture at identical concentration of MBBA. Inset: Plot of intensity vs inverse of temperature (1000/T) (K⁻¹) along with a linear fit (blue line) for peak I marked by a square.

The role of Entropic and Enthalpic Forces on the macroscopic and microscopic phase transitions of Liquid Crystals:
5.5. Phase Transition of Nematic Liquid Crystal in presence of a Room Temperature Ionic Liquid: 

EMIF, I also use two other RTILs, one of which having the same cationic arrangement with different anionic structure as EMIF namely 1-ethyl-3-methylimidazolium tetracyanoborate ([$Emim]^+[TCB]$) and another one having different cationic and anionic composition as EMIF namely 1-butyl-1-ethylimidazolium tetracyanoborate ([$BmPyr]^+[TCB]$) to observe whether the similar experimental trend is followed in RTIL-MBBA mixture in general or is it specific for one particular system. The molecular arrangements of these RTILs are shown previously in Chapter 2.

5.5.1 Phase Transitions and Transition Kinetics in EMIF 

Pure MBBA has been found to be an entropy driven system, i.e. the N-I transition barrier is entropic in nature[105]. To convert this barrier to an enthalpic one, I propose to use EMIF with the expectation of some enthalpic interaction in the MBBA-EMIF system leading to a change from non-Arrhenius to Arrhenius behaviour. To this end, the first step is to investigate the phase transitions in EMIF to check (1) whether EMIF remains a liquid around the N-I transition of MBBA and (2) whether it shows Arrhenius behaviour, i.e., possesses a constant activation barrier. This becomes more important since some of the previous reported data indicate existence of non-Arrhenius behaviour in some imidazolium based ionic liquids[181]. The reason behind this is imidazolium cations also have many conformational states due to their inherent molecular anisotropy[182]. The anionic arrangement of a particular imidazolium based RTIL will also play a major role to decide the rate dependent thermal behaviour. If the anionic arrangements are rigid, then this will provide a constraint to the conformal motions of imidazole and the molecule will be forced to take up a particular conformation.

I have undertaken a detailed rate dependent calorimetric investigation to understand the phase behaviour of EMIF during heating and cooling scans. In Figure 5.6 (a), DSC thermograms (Excess specific heat capacity ($\Delta C_p(kJ/molK)$)) vs Temper...
5.5. Phase Transition of *Nematic* Liquid Crystal in presence of a Room Temperature Ionic Liquid:

Figure 5.6: (a) Differential Scanning Calorimetry (DSC) thermograms ($\Delta C_p$ vs $T$) for pristine *EMIF* during heating (black) and cooling (red) scans at scan rate of 10 K min$^{-1}$, with representative ‘solid-solid’ ($T_{ss}$), ‘melting’ ($T_m$) and ‘crystallization’ ($T_{cr}$) transitions shown. (b) DSC second heating scan (dotted line) compared with first heating scan (solid line) at the scan rate of 20 K min$^{-1}$. Peak for ‘solid-solid’ transition is absent in the second heating scan while the melting peak remains, indicating the metastable nature of ‘solid-solid’ transition and existence of true ‘melting’ process in *EMIF*.

nature (K) for pristine *EMIF* at heating and cooling rates of 10 K min$^{-1}$ are shown. All the representative melting ($T_m$) and ‘solid-solid’ ($T_{ss}$) transitions during heating scan and crystallization ($T_{cr}$) during cooling scan are shown by the arrows. The absence of any glass transition or supercooling components in the phase transitions clearly indicates the ‘strong liquid’ nature of *EMIF*. In Figure 5.6 (b), a second DSC heating scan following a first heating and cooling scan cycle at 20 K/min is shown which indicates the absence of the solid-solid transition in the second heating scan while the melting peak remains. This indicates the existence of true melting process in *EMIF* (signature of a ‘strong liquid’) and the metastable nature of the ‘solid-solid’ transition.

Having confirmed that only ‘melting’ and ‘crystallization’ are the stable transitions in *EMIF*, and that *EMIF* remains a liquid around the MBBA N-I transition, I proceed to study the kinetic behaviour of these transitions. Rate dependent DSC
study was performed by carrying out heating and cooling scans at energy transfer rates starting from 2 to 30 K min$^{-1}$. In Figures 5.7 (a) and 5.7 (b), DSC thermograms for the heating and cooling scans at various heating/cooling rates around the melting and crystallization transitions are shown. Kinetic process is evident as the peak transition temperatures progressively shift towards higher (lower) temperatures during heating (cooling) scans. The peaks become broader with increasing heating (cooling) rates. The $T_m$ and $T_c$ values are plotted with heating and cooling rates ($\beta$’s) and the representative plot is shown in Figure 5.7 (c). The intercept value on the temperature axis at $\beta = 0$ are found to be $\simeq 11.1$ K.

In Figure 5.7 (d), the Arrhenius plots for melting and crystallization are shown where the data points in both these transitions can be best fit by straight lines which indicates thermally activated behaviour of these phase transitions. The activation energies were obtained from the slope of these plots using

$$ln\beta = ln\beta_0 - \frac{E_a}{RT}$$

where $\beta$ = heating rate, $\beta_0$ = quasi-stationary heating rate, $R$ = universal gas constant, $E_a$ = activation energy and $T$ = transition temperature.

Comparable $E_a$ values of $(220 \pm 17.7)$ and $(227\pm18.5)$ kJ/mol for melting and crystallization, respectively, are found. This activated Arrhenius nature strongly reflects the existence of enthalpic activation barrier in $EMIF$.

### 5.5.2 Phase Transitions in $MBBA$-$EMIF$ Mixtures: Screening and Self-screening

In order to investigate the role of $EMIF$ on the phase transition of $MBBA$, I have carried out a detail DSC study for $MBBA$-$EMIF$ mixtures at the heating rate of 10 K/min. Standard aluminium crucibles with $\sim$5 mg sample were used in each case.
5.5. Phase Transition of *Nematic* Liquid Crystal in presence of a Room Temperature Ionic Liquid:

![Diagram](image)

Figure 5.7: Rate dependent DSC thermograms for pristine *EMIF* during (a) heating and (b) cooling with the heating (cooling) rates ($\beta$) of 2 (solid, black), 5 (dash, red), 10 (dot, blue), 15 (dash-dot, purple), 20 (dash-dot-dot, pink), 25 (dash-dot-dot, orange) and 30 (- - -, green) K min$^{-1}$, respectively. (c) Plot of $T_c$ vs $\beta$ during heating (melting, triangles) and cooling (crystallization, circles) scans respectively with linear fits (lines). The temperature intercept at quasi-stationary $\beta = 0$ is large ($\sim 11.1$ K, arrow) suggesting strong *first order* character. (d) Natural logarithm of ramp rate (ln $\beta$) vs inverse of temperature (K$^{-1}$) or Arrhenius plots during heating (triangles) and cooling (circles) along with linear fits (solid lines).

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The role of Entropic and Enthalpic Forces on the macroscopic and microscopic phase transitions of Liquid Crystals:
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The crucibles were discarded after each scan thus removing the possibility of thermal history of the sample from affecting the subsequent scans. In Figure 5.8 (a), DSC thermograms for the mixtures of MBBA with 9 different concentrations ($C$) of EMIF starting from 0.01 to 2.4 mol% are shown during heating scans around the vicinity of the $N-I$ transition of MBBA. A peak in the plot, signifying a phase transition was found in each case with the corresponding transition temperatures decreasing quadratically with increasing EMIF concentration, coming to a saturation before the mixture became unstable after 2.4 mol% of EMIF, as shown in Figure 5.8 (b). A similar instability is seen below 0.9 mol% during cooling. The sharpness of the transitional peak also reduces with increasing RTIL concentration.

The results obtained from the calorimetric measurements are compared with an independent measurement which involves the microscopic detection of the $N-I$ phase transition temperature in the mixtures using a hot plate. This is usually done through optical polarization microscopy using a polarization microscope (IX70, Olympus, Japan) equipped with a $20 \times$ objective lens and a CC camera ($640 \times 480$ pixels) which is attached with a locally made hot plate stage. The mixture samples of MBBA-EMIF were placed on the hot plate stage and temperature was slowly raised until it crosses the nematic-isotropic clearing temperature. The minimum resolution of the instrument is 0.1 K. In this experiment the $I$ phase of a pure LC emerges from the $N$ phase as a ‘clearing’ or change from a characteristic texture of the microscopic image to a uniformly dark field of view at $T_{NI}$. Thus $T_{NI}$ is also referred to as ‘clearing temperature’. In the mixtures, it should be mentioned that while the ‘clearing temperatures’ were unambiguously detected, the phase from which the $I$ phase emerged, showed up (Figure 5.8 (b)(2)) as a much less textured field than that of the $N$ phase in pristine MBBA (Figure 5.8 (b)(1)), indicating a drastic reduction in the conformational disorder in the LC. Hence, I denote the phase transition temperature of the mixtures as $T_c$ rather than $T_{NI}$, and present the variation of $T_c$ thus
obtained beside the thermally obtained values in Figure 5.8 (b). The optical values also decrease quadratically, with a high rate at low RTIL concentrations, and then saturate. In Figure 5.8 (c), the measured enthalpy ($\Delta H$) of transition obtained for these mixtures from the DSC thermograms are plotted against $C$ for the heating scan.

This general quadratic nature of $T_c(C)$ and $\Delta H_c(C)$ indicates a MBBA intermolecular potential that is screened by the EMIF counterions along with ionic self-screening. Thus, to explain these data, I propose a simple charge screening and self-screening model according to which I assume that only the component ions of EMIF are active in both screening of the MBBA molecular quadrupoles and in self-screening while other forces (such as, dispersion forces) play no role, giving both $T_c$ and $\Delta H_c(C) \sim 1/C$. The saturation at comparatively higher RTIL concentration can be explained from the self-screening. In this model, I assume an effective charge $q$ located at each MBBA molecule screened by the counterions of EMIF surrounding the specific charge locations of the molecular quadrupole. If I further assume that addition of the small amount of ionic liquid only changes the value of $q$ keeping the other factors, especially the intermolecular separations, unchanged, then increase in $C$ will lead to more screening and hence to a lowering of $q$ ($q = k_1/C$). However, this process will generate its own self-screening and the final relation between $C$ and $q$, with all other factors such as intermolecular separation being lumped into two constant terms $k_1$ and $k_2$, is given by

$$C = \frac{k_1}{q} \left(1 - \frac{k_2}{q}\right) \quad (5.6)$$

leading to

$$T_c = T_c^0 + \frac{A_T}{C^2} - \frac{B_T}{C} \quad (5.7)$$

and

$$\Delta H_c = \Delta H_c^0 + \frac{A_H}{C^2} - \frac{B_H}{C} \quad (5.8)$$

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Table 5.1: Phase transition parameters (macroscopic and microscopic) for MBBA-EMIF mixtures (Data in arbitrary units if not mentioned otherwise, see text for details)

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Technique</th>
<th>Critical Value for Pristine MBBA (from fit)</th>
<th>Self-Screening Co-efficient (A_i)</th>
<th>Screening Co-efficient (B_i)</th>
<th>Threshold Ratio (C_i = \frac{2A_i}{B_i} (mol %))</th>
</tr>
</thead>
<tbody>
<tr>
<td>T_c</td>
<td>DSC</td>
<td>303.9</td>
<td>(-5.8 \pm 1.5) \times 10^{-1}</td>
<td>-0.71 \pm 0.15</td>
<td>0.06</td>
</tr>
<tr>
<td>T_c</td>
<td>PM</td>
<td>310.2</td>
<td>(-27 \pm 1.5) \times 10^{-3}</td>
<td>-1.53 \pm 0.55</td>
<td>0.05</td>
</tr>
<tr>
<td>\Delta H_c</td>
<td>DSC</td>
<td>0.22 \pm 0.08</td>
<td>(-5.1 \pm 0.08)</td>
<td>-1.88 \pm 0.18</td>
<td>0.54</td>
</tr>
<tr>
<td>\Delta I_c</td>
<td>FTIR</td>
<td>-11.5 \pm 3.8</td>
<td>(-9.0 \pm 3.8)</td>
<td>-40.5 \pm 8.3</td>
<td>0.44</td>
</tr>
</tbody>
</table>

where A_i, B_i (i = T, H) are the constants for self-screening and screening for T_c and \Delta H_c, respectively, and T_c(\Delta H_c) \rightarrow T_c^0(\Delta H_c^0) at C = 0. The threshold concentration for the self-screening is obtained from dT_c/dC = 0 and d\Delta H_c/dC = 0 to be 2A_i/B_i.

As seen in Figure 5.8 (b) and 5.8 (c), this model explains both the thermally and optically measured T_c(C) and the thermally obtained \Delta H_c(C). The values of the constants in Equation 5.7 and 5.8, obtained from the fits shown in Figures 5.8 (b) and 5.8 (c) respectively, are presented in Table 5.1.

To verify the consistency of the present model, similar measurements were performed for MBBA in presence of ([Emim]^+[TCB]^-) ([BmPyrr]^+[TCB]^-) taking the similar concentrations of these RTILs. The concentrations of these RTILs are varied similarly as in EMIF. The plot of T_c vs C is shown in the Fig 5.9 where the data points are well fit according to our screening and self-screening model. The fitting parameters along with the threshold concentrations of self-screening are shown in Table 5.2. This indicates that our proposed model is independent of the choice of RTIL and hold good for for every RTIL-MBBA mixtures in general.

Table 5.2: Phase Transition parameters for MBBA-RTIL mixtures

<table>
<thead>
<tr>
<th>RTILs</th>
<th>T_C^0</th>
<th>A_i</th>
<th>B_i</th>
<th>(C_i = \frac{2A_i}{B_i} (mol %))</th>
</tr>
</thead>
<tbody>
<tr>
<td>[BmPyrr]^+[TCB]^-</td>
<td>301.8</td>
<td>0.5 \pm 0.08</td>
<td>4.4 \pm 0.50</td>
<td>0.22</td>
</tr>
<tr>
<td>[Emim]^+[TCB]^-</td>
<td>303.2</td>
<td>1.4 \pm 0.23</td>
<td>3.04 \pm 0.51</td>
<td>0.92</td>
</tr>
</tbody>
</table>

The role of Entropic and Enthalpic Forces on the macroscopic and microscopic phase transitions of Liquid Crystals:
5.5. Phase Transition of Nematic Liquid Crystal in presence of a Room Temperature Ionic Liquid:

Figure 5.8: (a)DSC thermograms (heating scans) for the mixtures of MBBA-EMIF across the phase transition temperature (clearing temperature, \(T_c\)). EMIF concentrations \((C)\) are indicated as filled triangles (0.01 mol%), circles (0.6 mol%), squares(0.9 mol%), up triangles (1.2 mol%), down triangles (1.5 mol%), right triangles (1.8 mol%), left triangles (2.1 mol%) and diamonds (2.4 mol%). (b) Variation of \(T_c\) with \(C\), \(T_c(C)\), from polarization microscopy (circles) and DSC (up triangles) with fits (red lines) from the charge screening model (see text). Polarization microscopic images of (1) pristine MBBA and (2) MBBA-EMIF 0.9 mol% mixture below \(T_c\). (c)\(\Delta H_c(C)\) during heating (circles) fit with the model (line). (d) Arrhenius plots for MBBA-EMIF mixtures for 0.6 mol% (circles) and 2.1 mol% (triangles) EMIF concentration during heating, along with linear fits (lines). Inset: The same for pristine MBBA (squares) along with linear fit (line) and fit according to the monomolecular growth function (dotted line). (e) Plot of the obtained activation energy \((E_a)\) versus \(C\) with the fit according to our proposed screening and self screening model. (f) Calculated variation of average separation \((l_{EMIF})\) between EMIF molecules versus EMIF mole fraction \((x_{EMIF})\) with open circles corresponding to typical values of \(x_{EMIF}\).

The role of Entropic and Enthalpic Forces on the macroscopic and microscopic phase transitions of Liquid Crystals:
5.5. Phase Transition of Nematic Liquid Crystal in presence of a Room Temperature Ionic Liquid:

Figure 5.9: Variation of $T_C$ with RTIL concentration (C) where RTILs are represented by down triangles ([Emim]$^+$/[TCB]$^-$) and up triangles ([BmPyrr]$^+$/[TCB]$^-$). Data points are fitted with the proposed screening and self-screening model (see text for details) which are indicated by the blue and red lines.

5.5.3 Phase Transition Kinetics in MBBA-EMIF Mixtures

To investigate whether any change in the nature of the entropic activation barrier of MBBA takes place in presence of EMIF, I extracted Arrhenius plots ($1000/T$ (K$^{-1}$) vs ln $\beta$) for the mixtures at aforementioned molar ratios, from the rate dependent DSC studies and for the sake of simplicity only two of these are presented in Figure 5.8 (d) for comparatively low (0.6 mol%) and high (2.1 mol%) concentrations of EMIF. It is clear that these are linear plots and the best fits are shown by the continuous straight lines, indicating Arrhenius behaviour with a constant Activation Energy ($E_a$) for a particular EMIF concentration, as obtained from Equation 5.5. The obtained activation energies in the form of the slope of the graph are (248.9 ± 28.7) and (275.8 ± 31) kJ/mol for the EMIF concentrations of 0.6 and 2.1 mol% respectively. Similar plots were made for other EMIF concentrations (not shown) and activation energies were calculated from the slope of the graph in accordance with equation 5.5. In each case these plots exhibit activated Arrhenius behaviour. In
the previous chapter I have shown through rate dependent DSC studies that pristine MBBA exhibits non-Arrhenius behaviour over a broad ramp rate region (from 2-30 K/min). In the present situation for the detection of the transition temperature for MBBA-EMIF mixtures the measurements were carried through comparatively lower ramp rates of 2-10 K/min. Since this covers only a small portion of the large ramp rate window (2-30 K/min)over which MBBA exhibits non-Arrhenius feature, i.e., non-linearity, it looks like a linear curve and does not reflect the true non-Arrhenius feature. To test this out, Arrhenius plot for pristine MBBA was made in between the ramp rate 2-10 K/min and fit to straight line (solid line) as shown inset Figure 5.8 (d). The slope of the straight line was obtained to be \(-150 \pm 27.1\) (in the units of \(\frac{E_a}{R}\)). Relatively large standard deviation values indicate that this plot is indeed not a linear plot even in the lower ramp rate. However, the plot can best fit by a monomolecular growth function (dotted line) as described in the previous chapter. This indicates that introduction of EMIF concentration as low as 0.6 mol% is enough to cause the the drastic change in the molecular behaviour of MBBA from non-Arrhenius to Arrhenius.

The dependence of \(E_a\) on \(C\) is shown in Figure 5.8 (e), where the value of \(E_a\) is plotted. An increase of \(E_a\) with increase in \(C\) is observed initially from 0.6 to 1.5 mol% of EMIF concentration. After that concentration, a saturation behaviour in \(E_a\) is observed, the concentration from where self-screening becomes important. The values of \(E_a\) with \(C\) were fitted according to our proposed screening and self-screening model given as

\[
E_a = E_a^0 + \frac{A_E}{C^2} - \frac{B_E}{C} \tag{5.9}
\]

where, as before \(A_E\) (\(B_E\)) is the coefficient for self-screening (screening) and \(E_a^0\) is the activation energy at \(C = 0\). This model fits well with the data points further validating the applicability of our model.

A related fundamental question regarding this is the arrangement of the EMIF
ions around the MBBA molecules which is responsible for the screening effect. If I assume a hypothetical average specific volume $v_{EMIF}$ for the component ions of EMIF and a specific volume of $v_{MBBA}$ for MBBA, then I get the values $v_{EMIF} = 351.66$ Å$^3$ and $v_{MBBA} = 431.64$ Å$^3$, from their respective molecular weights and densities. I then assume the average specific volume of a ‘molecule’ of the mixture $v_{mix}$ to be a linear combination of its components as $v_{mix} = (1 - x_{EMIF})v_{MBBA} + x_{EMIF}v_{EMIF}$, with $v_{mix} = v_{MBBA}$, when $x_{EMIF} \equiv EMIF$ mole fraction = 0 and $v_{mix} = v_{EMIF}$, when $x_{EMIF} = 1$. This reduces to

$$v_{mix}(x_{EMIF}) = -79.98(x_{EMIF}) + 431.64$$

in units of Å$^3$ for the average volume per EMIF molecule in the MBBA-EMIF system.

If I consider that component ions of EMIF are distributed uniformly throughout the MBBA matrix, each centered in a spherical unit cell, then the volume can be calculated as

$$v_{mix} = x_{EMIF} (\pi l^3/6)$$

, where $l$ is the mean separation between the component ions of EMIF. The volume of the unit cell times the number of EMIF molecules gives the total sample volume divided by the total number of molecules. Equating the value of $l$ from this definition I get

$$l = [(6/\pi)(v_{mix}(x_{EMIF}))/ (x_{EMIF})]^{1/3} \quad (5.10)$$

Figure 5.8 (f) shows $l$ as a function of $x_{EMIF}$. For $l$ smaller than the length scale of the quadrupolar MBBA-MBBA interaction, the screening effect on this interaction potential should be dominant. The average molecular length for MBBA is $\sim 18$ Å. Hence, $l < 18$ Å for screening to be effective and, from Equation 5.10, the minimum $x_{EMIF}$ at which this happens is $\sim 0.12$ (circle enclosed by square box in Fig. 5.8 (f)), which is one order of magnitude higher than the experimental observation. Hence, the
assumed spherical arrangement of \textit{EMIF} ions around the \textit{MBBA} molecules has to be replaced by an anisotropic distribution to account for the quick initiation of screening. Since \textit{MBBA} molecules behave as a rigid linear quadrupole with $+2\delta$ charge localized over the imine nitrogen and $-\delta$ charges on each of the two benzene rings, I propose that component anions and cations of the \textit{EMIF} will surround the imine bond and the benzene rings and thereby initiate the screening, whereafter with increase in $C$ these will also form the centres for the self-screening. Since the component anions and cations have a large spread, the self-screening initiates at as low as 0.6 mol\% of \textit{EMIF} concentration.

5.5.4 Molecular Basis of Arrhenius Behaviour in \textit{MBBA-EMIF} Mixture

From the above discussion based on differential scanning calorimetry, it is verified that the Coulombic screening of \textit{MBBA} quadrupoles by the component ions of \textit{EMIF}, accompanied by ionic self-screening, is responsible for bringing in the Arrhenius behaviour in the ‘\textit{N-I}’ transition of \textit{MBBA}. I have shown in Chapter 4 that the out-of-plane distortions of the benzene rings in \textit{MBBA} cause conformational disorder whereby the imine bond dipole and the molecular quadrupole suffer random orientational changes. These are responsible for its observed non-Arrhenius behaviour. Thus the conversion from non-Arrhenius to Arrhenius behaviour in presence of \textit{EMIF} ions is expected to reduce this conformational disorder through a suppression of the out-of-plane motion initiated by large amplitude torsions. This leads to a reduction in the intensity of the out-of-plane distortions bands of the rings and subsequent increase in the orientational order in the imine dipoles (bringing them to the same molecular plane) leading to an increase in the imine stretch band intensity of \textit{MBBA} in presence of \textit{EMIF}. Moreover, the suppression of distortion affects directly the derivative of transition dipole moment with regard to the corresponding normal co-ordinate while the
orientational ordering increases the number of imine dipoles undergoing transition. Thus the intensity variation for the out-of-plane distortion modes is expected to show a non-linear dependence on $C$, consistent with the screening and self-screening model, whereas the intensity of the imine stretch mode would show a linear dependence.

Figure 5.10 (a) shows an initial sharp decrease with $C$ in the intensity of the out-of-plane distortion vibrations of both the benzene rings, which gradually saturates at 1.2 mol%. Interestingly, a red shift in the peak position of the band from 836 (888) cm$^{-1}$ for pristine MBBA to 832 (886) cm$^{-1}$ for MBBA-EMIF mixture is also observed. This indicates co-planarity of the rings further confirming the lowering of out-of-plane motions and hence, also of the reduction in the conformational disorder of MBBA and the ability to take up a fixed conformation in presence of EMIF. Figure 5.10 (b) shows a gradual increase in the intensity of the imine stretch vibration at (1625 cm$^{-1}$) in presence of EMIF indicative of the increase in the orientational ordering due to the planar arrangement of imine bond arising out of the lowering of conformational disorder as discussed above. Thus highly correlated motion of imine stretch gives rise to enhancement in the intensity.

In Figure 5.10 (c), the integrated IR intensities for imine stretch and a typical out-of-plane benzene ring vibration (at 836 cm$^{-1}$ for pristine MBBA) are plotted against $C$. This figure shows that the stretch intensity variation of imine bond is best fit by a straight line whereas the intensity variation of the out-of-plane distortion vibration follows the same quadratic decay with $C$ as I observed for $T_c(C)$ and $\Delta H_c(C)$, confirming our model of screening and self-screening by the RTIL ions. In fact, the out-of-plane distortion data is fit by the same equation as

$$I_c(C) = I^0_c + \frac{A_I}{C^2} - \frac{B_I}{C}$$  \hspace{1cm} (5.11)

the values of the self-screening and screening parameters, $A_I$ and $B_I$ as well as the threshold ratio $2A_I/B_I$ as obtained from the fit of this equation to the data are also

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The role of Entropic and Enthalpic Forces on the macroscopic and microscopic phase transitions of Liquid Crystals:
5.5. Phase Transition of Nematic Liquid Crystal in presence of a Room Temperature Ionic Liquid: presented in Table 5.1, thus showing the applicability of the model at both microscopic and macroscopic length scales. In Figure 5.10 (d), the molecular structure of MBBA along with the imine stretch vibrations and out-of-plane vibrational modes for two differently substituted benzene rings are shown schematically.

5.5.5 Emergence of a New Ordered Phase in MBBA in Presence of EMIF?

The discussion based on calorimetric and spectroscopic study indicates that significant reduction in the out-of-plane distortion vibrations of the benzene rings in MBBA in presence of EMIF through screening may lead to the molecular ordering in MBBA. In MBBA, nematic order is possible due to the presence of many degenerate ground states at lower temperature which arise out of the different conformational motions at those temperatures. The existence of metastable phases in MBBA at lower temperature between glass phase and nematic phase has already been reported by various authors[102, 183, 184]. These authors also verified that the so called ‘Solid’ phase in MBBA is not truly ‘Solid’, i.e., crystalline in nature [185] and it has been identified as ‘plastic crystalline’ phase. Each of these ‘polymorphic phases’ can be regarded as composed of different conformational states of MBBA having equal or near equal energy. The results of our above study suggest that the number of these conformations are significantly reduced by enthalpic interaction with EMIF along with the reduction in the out-of-plane distortion vibrations of the benzene rings as the torsional motion of the rings is reduced. The expected result of this reduction in conformational entropy is that MBBA is forced to take up a particular conformation where the benzene rings will be coplanar with the imine group. This, in turn, will give rise to a phase that may be better ordered than the nematic phase of MBBA.

To verify this conjecture, I have employed DSC study for pristine MBBA and its mixture with EMIF at aforementioned concentrations around the ‘Solid-Nematic’
5.5. Phase Transition of *Nematic* Liquid Crystal in presence of a Room Temperature Ionic Liquid:

Figure 5.10: Fourier transform infrared (FTIR) spectroscopy of *MBBA-EMIF* around the (a) out-of-plane distortion vibrations of benzene rings (800-910 cm\(^{-1}\)) with \(C\) of 0.6 (solid), 0.9 (dash), 1.2 (dot), 1.5 (dash-dot), 1.8 (dash-dot-dot) and 2.1 (dash-dot-dot-dot) mol% where the two peaks correspond to the two differently substituted benzene rings in *MBBA* and (b) imine stretch vibration (1610-1660 cm\(^{-1}\)) with the symbols having the same meaning. (c) Plot of integrated IR intensity vs \(C\) for the imine stretch (triangles, left ordinate) and out-of-plane distortions of benzene rings (circles, right ordinate) along with linear fit for imine stretch (solid line) and fit according to the model for out-of-plane distortions (dotted line). (d) Schematic representation of the molecular structure of *MBBA* along with its different vibrational modes shown by arrows.
5.6 Concluding Remarks

In conclusion, in this chapter I have presented the results of my investigations on
the specific role of entropic force mediated through organic non-polar solvent hexane
and enthalpic force mediated through organic polar solvent methanol as well as RTILs
separately on the tunability of the N-I phase transition of a nematic liquid crystalline
molecule through calorimetric study and I have provided the molecular basis of the

The role of Entropic and Enthalpic Forces on the macroscopic and microscopic
phase transitions of Liquid Crystals:
observed change in the macroscopic quantities through spectroscopic investigations. The effect of these two distinct forces has been discussed in a simple and general way. I observe that while in entropic solvent, a continuous decrease in the transitional temperature and associated enthalpy, a saturation behaviour is observed after an initial decay in these parameters in presence of enthalpic solvents. This brings in the change in the transitional behaviour of nematic LC molecule in presence of these solvents. Although the dominant role of screening is found in both these cases, the self screening behaviour is observed only in case of enthalpic solvents. Also, the screening and self screening is found to initiate at much low concentration in RTILs compared to the organic dipolar solvent which shows the strength of charge screening compared to dipole screening. The most important aspect that has come out through our studies is that in entropic solvents, the non-Arrhenius nature of $N$-$I$ transition of nematic LC molecule is not only preserved but also enhanced, while enthalpic interaction with dipolar solvent and RTILs completely destroy this non-Arrhenius feature and make the system to follow activated Arrhenius behaviour. This change in the macroscopic behaviour has been investigated through the change in the molecular conformations through FTIR spectroscopy where the suppression in the out-of-plane torsion of the benzene rings about the C-C and C-N bonds are ultimately responsible for the observed change in the transition from non-Arrhenius to Arrhenius.