# Rheological Studies on Ionic Liquid Dispersions of Surfactant and Nanoparticles

by

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A thesis submitted to the Board of Studies in Physical Sciences in partial fulfilment of requirements for the degree of

# **DOCTOR OF PHILOSOPHY**

**O**f

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## DECLARATION

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(K. Saravanakumar) Ph. D Candidate **Dedicated** to

All

**Research Scholars** 

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#### **CHAPTER 1**

#### **INTRODUCTION**

Many fluids of everyday experience like milk, blood, ink, paint, foam, smoke, fog, clay suspension etc. are colloidal dispersions. Colloidal dispersion can be defined as the dispersion of mesoscopic particles (dispersion phase) of one material in other material (dispersion medium). Mesoscopic scales range from a few nanometers to a few microns. It is not necessary that all the three dimensions of the colloidal particles should possess mesoscopic scales. In the case of fibres, only two dimensions are in mesoscopic scale. Based on the state of dispersion phase and medium, colloidal dispersions can be divided into suspensions, emulsions, aerosols, foams etc.

Due to thermal energy, colloidal particles undergo Brownian motion in dispersion. While executing Brownian motion, these particles may come closer and flocculate due to attractive van der Waals interactions. Colloidal dispersions can be stabilized in two ways. A thin polymer layer (~ 1 nm) is adsorbed or grafted on to the surface of the colloidal particles. This way of stabilizing colloidal particles is called steric stabilization (Fig. 1.1 (a) & (b)). Aqueous suspensions of poly(methyl methacrylate) (PMMA) is a good example for sterically stabilized suspensions. Some moieties present in the molecules of colloidal surface get dissociated into the dispersion leaving the colloidal surface charged. This type of charging the colloidal surface prevents flocculation due to electrostatic repulsion and is known as charge stabilization (Fig. 1.1 (c)). Aqueous suspension of silica particles and polystyrene particles is a good example for charge stabilization.



Fig. 1.1 Stabilization of colloids through (a) adsorbed polymer, (b) grafted polymer and (c) charges

1.1 Structural ordering in colloidal systems: Colloidal crystals and glasses Monodisperse colloidal particles in a solvent under appropriate conditions exhibit crystalline, liquid-like, glass-like ordering [1-5] analogous to that of atomic systems. For instance, charge stabilized colloidal dispersions undergo crystallization at a volume fraction ( $\phi$ ) ~ 0.005 whereas sterically stabilized dispersions undergo at a volume fraction ( $\phi$ ) ~ 0.5 [2, 5]. Like atomic systems, in colloidal systems (charge stabilized) too, transitions between various states are possible by changing the salt concentration [2, 5]. The value of elastic constants and the latent heat of melting for colloidal crystals are remarkably close to that of atomic systems [2, 6]. The time scales associated with diffusion in atomic systems are of the order of nanoseconds to microseconds. Since, the size of the colloidal particles is three orders of magnitude greater than that of atoms, their time scales of diffusion is of the order of microseconds to seconds. All these comparisons convince one to consider colloidal systems as scaled up versions of atomic systems as well as an appropriate model system to study phase transition studies such as crystallization, glass transition, phase separation etc. [3, 5]. Colloidal dispersions exhibit in glassy state at high volume fractions. A homogenous, non-ergodic colloidal dispersion having liquid like structure, whose elasticity rooted from caging of one particle by neighboring particles, is called as colloidal glass [7]. The state of the colloidal glass is metastable and hence exhibits aging. Colloidal glasses are homogenous over interparticle distances. Hard sphere colloids exhibit glassy behavior at volume fractions ranging between 0.58 and 0.64 and at much lower volume fractions (~0.005) in the case of charged colloids [2].

#### 1.2 Colloidal gels and Nanocomposites

#### 1.2.1 Colloidal Gels

Colloidal dispersions with strong ( $U_o/k_BT$ >> 1, where  $U_o$  is the depth of the attractive potential) attractive interactions lead to gelation [8]. Colloidal gels are three dimensional disordered networks of aggregated particles with solid like behavior and exhibit non-ergodicity. They are inhomogeneous over length scales of the network,  $\xi$  (mesh size). For the networks to be elastic on a typical observation time scale, the necessary condition is that the lifetime of junction point is sufficiently long. The life time of junctions will be long if  $U_o/k_BT$ >>1 [8].

Colloidal gelation can happen through two modes, diffusion limited cluster aggregation (DLCA) and reaction limited cluster aggregation (RLCA). In the case of DLCA mode, the gelation is fast and each collision among the colloidal particles results in aggregation whereas in RLCA mode, the gelation is relatively slow and only a fraction of the collisions results in particle aggregation [9].

#### 1.2.2 Rheology of Colloidal Gels

Colloidal gels exhibit two types of rheological behavior namely strong gels and weak gels based on the interaction between the particles is strong or weak. In the case of strong gels the elastic modulus, G' is independent of the applied frequency, greater than the viscous modulus, G'' and the difference between them is high (G''/G' < 0.01) as shown schematically in Fig.1.2. In the case of weak gels, G' exhibits weak frequency dependence, greater than G'' and the difference between them is not high (G''/G' > 0.01).



Fig. 1.2 Schematic representation of rheological behavior of colloidal gels

Colloidal gels have typical yielding behavior as shown in the Fig.1.3. Upon increasing the stress/strain amplitude, G'' increases, reaches a maximum and then falls. This distinct peak exhibited by G'' is an important rheological property of colloidal gels [10].

It would be interesting to compare the colloidal gels with polymer gels. In contrast to the colloidal gels, polymer gels are formed from the crosslinking of polymer chains through covalent bonds or physical bonds like vander Waals interactions. Colloidal gels fracture at low strains as compared to polymer gels. Also, colloidal gels have poor reproducibility and very short linear response as compared to polymer gels [11].



#### Strain amplitude

Fig. 1.3 Schematic representation of yielding behavior of colloidal gels

#### 1.2.3 Nanocomposites

Nanocomposites are composite materials in which one or more components have nano dimensions. The purpose of adding nanosized components to a matrix material is to enhance certain properties like mechanical strength (stiffness and strength) [12], thermal conductivity [13] etc. Many polymer materials showed enhanced mechanical stability upon adding nanoparticles and are called polymer nanocomposites. This is because of the high surface to volume ratio of the nanoparticles as compared to bulk [12]. Examples include polymer/clay nanocomposites, polymer/layered silicate nanocomposites, rubber/clay nanocomposites, fullerene/carbon nanotube composites etc.

#### **1.3 Micellar Systems**

One of the important types of colloidal systems is association colloids which are formed by self aggregation of certain type of molecules called surfactants or amphiphiles. This self assembly of surfactant molecules is thermodynamically driven and these structures are called micelles.

#### **1.3.1** Aqueous surfactant systems

Surfactants are amphiphilic molecules having both hydrophilic and hydrophobic parts. The hydrophilic part normally contains charged ions or polar head groups whereas hydrophobic part contains hydrocarbon chains. Surfactant molecules are surface active i.e. they reduce the surface tension of the solvent. It is known that surface tension arises from the cohesive force between the molecules of a solvent at interface. When dissolved in solvent, these surfactant molecules adsorb at the interface which reduce the cohesive forces between the solvent molecules effectively and hence the surface tension of the solvent. When surfactants are dissolved in water, they are called aqueous surfactant solutions.

Based on the type of head group, surfactants are classified into ionic, non-ionic and zwitterionic. Ionic surfactants are further classified into cationic and anionic. If the head group of the surfactants carries positive charge, then they are called cationic surfactants. Examples are Cetyltrimethyl ammonium bromide (CTAB). Cetylpyridinium chloride (CPC), Dioctadecyldimethylammonium bromide (DODAB) etc. If the head group of the surfactants carries negative charge, then they are called anionic surfactants. Examples sodium dodecyl sulfate (SDS), are perflurooctanesulfonate (PFOS), alkyl benzene sulfonates etc. If the head group of the surfactants does not carry any charge, then they are called non-ionic surfactants. Examples are Polyoxyethylene glycol alkyl ethers (Brij-35 & 700), Triton X-100, Polyoxypropylene glycol alkyl ethers. If the head group of the surfactants carry both positively charged and negatively charged moieties, then they are called Zwitterionic surfactants. Examples are long chainaminoacids, sulphobetaine type surfactants, etc.

#### Micelles

When surfactants dissolve in water, the surfactants molecules get adsorbed at the interface, due to the repulsive hydrophobic interaction of the alkyl chains of the surfactant with water. Upon increasing the concentration further, a situation is reached where the interface is saturated with surfactant molecules. Beyond this concentration, the surfactant molecules self aggregate in such a way that their hydrophilic head groups point towards water, whereas their hydrophobic tails point inwards in order to minimize the water interaction which in turn minimizes the free energy. These self aggregated structures of surfactants are called micelles and the concentration at which these structures are formed is termed as critical micelle concentration (CMC).

#### **Identification of CMC**

The physical properties of surfactant solutions like, electrical conductivity, surface tension, osmotic pressure, turbidity etc. vary abruptly beyond critical micelle concentration (CMC). This change in physical property is used to determine the CMC of surfactant solutions. When these properties are plotted against the concentration of the surfactants, a clear change in slope is seen at CMC as shown in Fig. 1.4.



Fig. 1.4Schematic representation of various physical properties of surfactant solutions as a function of surfactant concentration

Surface tension studies are generally used to estimate the CMC of surfactant solutions. Surface tension decreases upon increasing the concentration of surfactants and remains constant after CMC (Fig. 1.4). In the case of ionic surfactants, electrical conductivity studies are widely used to determine CMC [13]. Electrical conductivity changes at CMC due to the binding of counterions with the micelles. Turbidity increases significantly beyond CMC as micelles scatter more light compared to surfactant monomers [14]. Osmotic pressure increases gradually upon increasing the surfactant concentration and the rate of increase is negligible after CMC.

#### **Phase diagrams of Surfactants**

Micelles formed beyond CMC are known to have shapes either spherical, cylindrical or double layered which is shown schematically in Fig. 1.5. Spherical micelles contain hydrophilic part on their surface facing water whereas hydrophobic part faces the interior. Spherical micelles are formed in the concentration range slightly above the CMC. Upon increasing the concentration of the surfactant further, these



Fig. 1.5 Different shapes of association of surfactants (a) spherical micelles, (b) cylindrical micelles and (c) bi-layer

may grow to cylindrical micelles. The structure of micelles depends upon many factors like concentration, geometry and chemical structure of the surfactant, surfactant-water interaction, temperature etc. The formation of micelles in aqueous solution is strongly dependent on the solution temperature and concentration of the surfactant. The minimum temperature required for the self-aggregation of surfactant molecules into micelles in a solution is called Kraft temperature. Below this temperature, surfactants will be dispersed as monomers only. Generally, the critical micellar concentrations of aqueous surfactant systems are low. Also, spherical micellar phases and rod-like micellar phases occur at a narrow concentration range. But there are many other phases like liquid crystalline phases which can be formed upon increasing the concentration of the surfactants. The following phase diagram (Fig. 1.6) depicts the different phases of the binary mixture of surfactant, dodecyl trimethylammonium chloride and water [14].



Fig. 1.6 Binary phase diagram of cetyltrimethylammonium chloride and water as a function of surfactant concentration and temperature (adopted from [14]). *mic,cub,hex* and *lam* represent micellar, cubic, hexagonal and lamellar phases respectively.

When the concentrations are increased to higher value, various liquid crystalline phases are formed due to intermicellar interactions. Out of the various phases formed, three phases namely, lamellar, hexagonal and cubic has been well studied and established [14]. It should be noted here that the phases formed is dependent on the type of the surfactants and solvents used and also the temperature. All aqueous surfactant systems which form micelles do form liquid crystalline phase. There are certain aqueous surfactant systems which do not form micelles but form liquid crystalline phases. Hence, formation of liquid crystalline phases is universal for aqueous surfactant solutions [15].

#### Effect of added Salt and Temperature on micellar growth

The addition of salt to a surfactant solution significantly reduces the CMC in the case of ionic surfactants. The added salt by getting adsorbed onto the micellar surface reduces the electrostatic repulsion between the head groups of the surfactant molecules in micelles and paves the way for micellar growth. Also, the added salt enhances the growth of micelles in such a way that spherical micelles grow to rod-like and then to worm-like micelles [16].

Not all salts enhance growth. For example, in the case of aqueous SDS (anionic surfactant) solutions, the inorganic salt LiCl has no significant effect on micellar growth [14]. On the other hand, other salts like NaCl, KCl etc. enhance the micellar growth and significantly reduce the CMC in aqueous surfactant solutions. For eg, in aqueous SDS surfactant solutions, when the concentration of NaCl is > 0.45M, spherical SDS micelles grow to rod-like micelles [17]. Similarly, addition of organic salt with aromatic ring (hydrotropes) also effects the micellar growth [18, 19]. Some examples for micellar growth upon addition of organic salt are the growth of SDS micelles upon addition of *p*-toluediene hydrochloride [18] and growth of CTAB micelles upon addition of sodium salicylate [20].

It is known that temperature has a mild effect on CMC of aqueous surfactant solutions. However, CMC of ionic surfactants shows an increase at higher temperatures

[14]. In the case of non-ionic surfactants, surfactants phase separate from aqueous phase upon increasing the temperature. The temperature at which this phase separation occurs is called cloud point. This phase separation is attributed to the increased hydrophobic interactions between the hydrocarbon chains upon increasing the temperature.

#### **Rheology of aqueous surfactant solutions**

The viscosity of the aqueous surfactant solutions having concentration less than CMC (i.e. the solution contains only surfactant monomers) is almost equal to the viscosity of the solvent itself. This is because the dimension of the surfactant monomers is of the order of angstroms which will not influence the flow behavior of the solvent.

When the concentration of the surfactants is equal to CMC or slightly above than that, surfactants aggregate to form spherical micelles. In this case, it can be modeled to a colloidal dispersion and hence the viscosity can be explained according to the expression,

$$\eta_{\rm s} = \eta_{\rm sv} (1 + 2.5\phi) \tag{1.1}$$

Where  $\eta_{sand} \eta_{sv}$  are the viscosities of solution and solvent respectively and  $\phi$  represents volume fraction of the micelles. The viscosity of the aqueous solutions containing spherical micelles is greater than the viscosity of the solvent with Newtonian behaviour. This is because the dimension of the spherical micelles is of the order of a few nanometers which influence the flow behaviour of the solvent.

Spherical micelles can grow to rod like micelles and then to wormlike micelles in aqueous surfactant solutions either by increasing the surfactant concentration or increasing the salt concentration while keeping the surfactant concentration above CMC. A rod-like micelle is stiff throughout its length whereas a wormlike micelle is stiff only upto the persistence length and become flexible beyond that length. When the rod-like micelles are free and non-interacting in the solution, the viscosity of the solution is high compared to the solvent viscosity and continues to be a Newtonian liquid. When salt concentration is increased further, the rod-like micelles grow beyond the persistence length and form worm-like micelles. The entanglement of worm-like micelles results in abrupt increase in viscoelasticity of the surfactant solution. In this case, the worm-like micellar solution exhibits shear thinning behavior. Fig. 1.7 shows the schematic of mechanical spectrum of entangled worm-like micelles. At low frequencies the elastic modulus, G' is lower than the viscous modulus, G''. But at a characteristic frequency,  $\omega_s$ , G' crosses over G'' and with further increase of frequency, G'continues to dominate over G'' reaching a plateau value,  $G_o$ , The inverse



Fig. 1.7 Schematic representation of G'and G'' as a function of angular frequency,  $\omega$  for an entangled wormlike micellar system

of the frequency  $\omega_s$  is called the longest relaxation time,  $\tau_s$ . In general, all worm-like micellar solutions show single relaxation behaviour similar to entangled polymer solutions. The variation of  $G'(\omega)$  and  $G''(\omega)$  with  $\omega$  can be modeled by Maxwell's model [13] with single relaxation time,  $\tau$  and  $G'(\omega)$  and  $G''(\omega)$ can be expressed as,

$$G'(\omega) = G_0 \omega^2 \tau^2 / (1 + \omega^2 \tau^2); \qquad G''(\omega) = G_0 \omega \tau / (1 + \omega^2 \tau^2)$$
(1.2)

Where,  $G_o$  is the plateau modulus,  $\omega$  is applied angular frequency.

It should be noted here that though entangled worm-like micellar systems are often termed as "viscoelastic gels", characterized by a finite relaxation time, they differ from polymer gels in that, they have very long relaxation times [21].

#### **1.3.2** Non aqueous surfactant systems

Non polar solvents like *n*-heptane, *n*-octane, benzene, hexadecane, cyclohexane etc. favour micelle formation in a quite different way. The micelles in these solvents are called reverse micelles because the hydrocarbon tails of the surfactant molecules in the micelles are pointing towards the bulk of the solution whereas the polar head groups are pointing towards the core of the micelles in order to minimize the interaction with the non polar solvent. In contrast to aqueous systems, the aggregation number (no of surfactant molecules present in a micelle) of micelles is very small (~10) compared to water (~100) and as a consequence of this property, identification of CMC is difficult. In fact the physical properties of these inverse micellar systems vary gradually near CMC as compared to the abrupt change near CMC in the case of water. Hence, a precise value of CMC cannot be defined for non aqueous surfactant solutions.

However, only a few non aqueous solvents favor the formation of micelles similar to that of water. They are polar solvents like formamide, ethylene glycol, glycerol, N-ethylformamide etc. Like aqueous systems, the driving force for forming the micelles in these solvents is also the hydrophobic effect. However, the CMC of the surfactants in these solvents is higher when compared to water [19]. The effect of temperature on CMC for these solvents is also similar to that of water. Due to the lack of many solvents, studies on surfactant systems with non aqueous polar solvents as dispersion medium are limited. Recently, a new class of liquids called ionic liquids (ILs), which are polar in nature have been synthesized and are used as solvents for preparing micellar ionic liquids (MILs)*i.e.* dispersions of micelles in ionic liquids. Studies on MILs are given below.

#### 1.3.3 Surfactant systems with ionic liquids as solvents

Ionic liquids (ILs) are a class of organic salts with organic cations and inorganic/organic anions whose melting point is less than 100°C [22]. The advantages of ILs over the conventional organic solvents come from their unique physicochemical properties. They posses negligible vapour pressure, high thermal stability, high electrical conductivity, wide electrochemical window, ability to dissolve several complex compounds [23] etc. Due to the presence of electrostatic attraction between cations and anions, ILs have very low vapor pressures at ambient conditions and hence there is no pollution due to evaporation of ILs unlike the highly volatile organic solvents. Since only ions are present, the electrical conductivity of the ILs is very high of the order of mS/cm. Also, the electrochemical window of ILs is wide ranged. These properties prompt them to be used as green solvents for dissolving cellulose [24], chitin [25], surfactants [26] and other complex organic and inorganic compounds.

#### Local structures in ILs

Apart from the physical properties like high electrical conductivity, thermal stability etc., there are yet other properties which differentiates ILs from the conventional solvents. Presence of nanoscale spatial heterogeneities is one among them. Recent experimental and simulation studies on ILs reveal the presence of nanoscale local structural ordering of cations and anions [27]. Also, in the case of imidazolium ILs, the cation itself exists as two conformers [28]. When the alkyl chain length of the cations of ILs exceeds a particular value, liquid crystalline phases are also observed

[29]. Dynamic light scattering studies on imidazolium based ILs, show the presence of spatial heterogeneities with correlation lengths of the order of 100-200 nm and these structures were reported to be present even at elevated temperatures [30]. Even some researchers claim that ILs are in a state which is intermediate between solids and liquids. Many studies imply that the reason for the local ordering is due to the segregation of non-polar alkyl chains of cations in a polar environment inside the IL [31].

Though there have been many studies on the applications of ionic liquids as alternative green solvents to many organic solvents, studies on ionic liquids as solvents for surfactant self assembly is limited. Only, the ionic liquids, Ethylammonium nitrate (EAN) [32], BmimCl [25], BmimPF<sub>6</sub> [25] and EmimTFSI [33] were studied. However, in recent years, significantstudies have been carried out. Among these ILs, EAN is widely studied as a solvent for the self assembly of surfactants [34, 35, 36]. Anderson et al [25] have observed the self assembly of anionic surfactant SDS (sodium dodecyl sulfate), surfactants Brij 35 (polyoxyethylene docSS non ionic ether), (dioctylsulfosuccinate) SB3-10 (capryrylsufobetaine) in the IL BmimCl and Brij 35, Brij 700 and SB3-10 in the IL Bmim PF<sub>6</sub> using surface tension measurements.Pandeyet al studied the surfactants CTAB and non-ionic surfactants in the IL, EmimTFSI [33]. Interestingly, all the non ionic surfactants showed micelle formation. However, CTAB was not found to form micelle though it dissolves up to a concentration of 200mM in the IL [33].

All the above studies have certain commonalities. Self assembly of surfactants in ILs indicates the presence of solvatophobic interactions of ILs with the alkyl chains of the surfactants. The above mentioned surfactants formed micelles in ILs at a concentration greater the CMC of the same in water.

#### 1.4 Governing forces in colloidal and micellar systems

#### Hard sphere interaction

The hard sphere potential, U(r) between two neutral colloidal particles of radius, R separated by a distance, r in a dispersion is given by,

 $U(r) = \infty$  when  $r \leq R$ 

$$= 0 \text{ when } r > R \tag{1.3}$$

#### **Repulsive Electric double Layer forces**

In the case of aqueous dispersions of charged colloids or micelles of the ionic surfactants, the surface is charged. Due to the electrostatic attraction, the charges present on the surface attract the counter ions present in the bulk of the solution. This counter ions form a layer around the charged surface in such a way that the number of counterions decreases as we move away from the surface, resulting in a diffused electrical double layer. This leads to a repulsive interaction between two charged particles or micelles of radius, *R* having a surface potential  $\psi_{o}$ , with a condition,  $\kappa R < 3$ , which is given by the expression [37],

$$U(r) = 4\pi\epsilon R^2 \psi_0^2 \exp(-\kappa r) / (2R + r)$$
(1.4)

Where *r* is the closest distance of separation,  $\varepsilon$  is the permittivity of the solvent, *k* is the Boltzmann constant, *T* is the absolute temperature, where  $\kappa^{-1}$  is the thickness of the double layer given by the following expression,

$$\kappa^{-1} = (\epsilon kT/2n_0 z^2 e^2)^{1/2} \tag{1.5}$$

where k is the Boltzmann constant, Ze is the charge of the ion and  $n_o$  is the ionic concentration of the bulk solution.

#### Attractive van der Waals forces

Electrostatic interactions are confined only to charged systems like ions or charged surfaces. Hence these interactions are absent in neutral molecules and atoms. However, there are certain types of interactions of dipole origin, present universally in all atoms and molecules. They are collectively called as van der Waals interactions. These interactions are attractive interactions between atoms or molecules which arise from three different types of dipole interactions. They are i) interaction between two induced dipoles ii) interaction between two permanent dipoles and iii) interaction between one permanent dipole and an induced dipole.

van der Waals forces between two colloidal particles or micelles separated by a distance r (in units of particle size) is given by,

$$U(r) = -(A/12)[1/(r^2 - 1) + 1/r^2 + 2\ln(1 - 1/r^2)]$$
(1.6)

Where A is Hamakar constant.

#### **Steric forces**

When the surface of the colloidal particles is coated with a polymer layer either due to adsorption or chemically grafted, a repulsive force is produced as the polymer layers approach each other. This repulsive force is termed as Steric forces. The repulsive potential between two polymer coated colloidal particles in a given dispersion is given by [38],

$$\varphi_s = \left(akT\beta^2 \left(\frac{1}{2} - \alpha\right)\right) / H_s \nu \tag{1.7}$$

Where  $\alpha$  is the interaction parameter (should be lesser than  $\frac{1}{2}$ ),  $\beta$  is the thickness of the stabilized layer,  $H_s$  is a function of interparticle distance, polymer and system

characteristics, v is the volume of the solvent molecule, k is Boltzmann constant and T is temperature.

#### 1.5 Motivation for the thesis

Rheology of aqueous micellar systems is well studied. However, only a few studies are devoted to non aqueous polar solvents. This is due to the limited number of micelle favoring non aqueous polar solvents. However, as discussed earlier, ILs provide a new platform with a wide range of solvents with unique physical properties. Hence, studying the rheology of surfactants and nanoparticles is of considerable interest both from the fundamental point of view as well as applications point of view. With this as a motivation BmimCl (1 Butyl-3-methylimidazolium Chloride) ionic liquid is chosen as a solvent for studying the rheology of SDS micelles. It is an imidazolium based IL, whose melting point is  $\approx 68^{\circ}$ C. It is a protic IL from which other ILs of Bmim cation are derived. It is hygroscopic, hydrophilic and solid at room temperature; the supercooled form of this IL remains as liquid [14]. The striking feature of BmimCl is its ability to dissolve complex compounds, cellulose and chitin [8, 9]. Also, many ionic liquids possess surface active properties when dissolved in water. In order to investigate the surface active properties of this IL in water, surface tension measurements (Wilhelmy plate method) have been carried out. These studies are presented in chapter 3.

Anderson *et al* [25] have reported the formation of large size SDS micelles in BmimCl beyond a CMC of ~ 48mM. However they could not measure the size and shape either by light scattering or small-angle-neutron scattering (SANS) techniques due to large amount of scattering leading to the saturation of detectors [25]. Takada *et al* [37] have performed rheology experiments on BmimCl containing different concentrations of LiCl and observed abnormal increase in viscosity and shear thinning behaviour at high shear rates. Shear thinning behaviour is attributed to the existence of associative structures in BmimCl which undergoes change at high shear rates. The abnormal increase in viscosity is believed to arise from changes in the number and/or size of the large-scale association structure in BmimCl in the presence of LiCl [39, 30, 40]. However, there are no reports on the rheological behavior of BmimCl when LiCl and SDS are present. Further, the effect of temperature on the associative structures is also not well studied. Also, Takada *et al* did not study the dynamic rheological behaviour of the sample which is very important to qualify the state of the sample. Motivated by the above studies, the rheological, SANS and turbidity studies on SDS-BmimCl solutions with different amounts of LiCl as a function of temperature have been carried out and contributes chapter 4.

Having studied the rheology of micellar ionic liquid (IL with micelles of surfactant molecules), it is interesting to study the rheology of colloidal systems using ionic liquid as solvent. In the previous study, BmimCl was used as a solvent. However, BmimCl as a solvent has two drawbacks. The first one being it is in supercooled liquid state at room temperature with high viscosity (~20 Pa s). The second one is its high hygroscopic nature which requires careful handling during experiments and the dissolved water changes the solvent property. Hence it is important to seek an alternative non-hygroscopic IL which is liquid at room temperature. EmimTFSI is a non-hygroscopic room temperature ionic liquid whose melting point is  $-15^{\circ}$ C. Due to the low viscous nature, this ionic liquid is widely used as solvent in many applications [18].

Watanabe group have studied the viscoelastic behaviour of nanocomposite ion gels based on different weight percentage of silica nanoparticles and an ionic liquid, EmimTFSI at room temperature along with ionic conductivity studies [41]. They found that the nanocomposite transformed from liquid (1 wt%) to gel state (3 wt%) by increasing the concentration. However, the effect of temperature on these materials has not been studied. Motivated by the above studies, the rheological studies on silica-ionic liquid nanocomposites with different concentrations of silica nanopowder as a function of temperature have been carried out and contributes chapter 5.

#### 1.6 Outline and Important results of the thesis

This thesis presents the rheological studies as a function of temperature on BmimCl, Micellar Ionic liquid with varying salt concentration and Silica Ionic liquid Nanocomposite with varying concentration of silica nanoparticles along with other studies like small angle neutron scattering (SANS), surface tension and turbidity measurements.

The important findings of this thesis are as follows:

- The ionic liquid BmimCl has been synthesized and its rheological properties have been studied as a function of temperature. Flow measurements have revealed that it is a Newtonian fluid. The presence of non zero elastic modulus obtained beyond the melting point (68°C) by dynamic rheological measurements revealed the presence of dynamic network structures over a wide range of temperature.
- Surface tension measurements on aqueous BmimCl revealed that BmimCl does not form micelles in water.
- Highly viscous SDS-micellar ionic liquid (4.45 wt%) dispersions with different concentrations of LiCl salt 4.8, 9, 13.1&18.7 wt% have been prepared. Through detailed rheological study, for the first time, the sample with 18.7 wt% LiCl

concentration is shown to exhibit a weak gel state at high temperatures (< 80°C), and viscoelastic liquid state below 80°C. Usually viscoelastic liquid shows gelation upon cooling. But the present study constitutes an evidence for high temperature gelation.

- Small angle neutron scattering (SANS) measured on the micellar-ionic liquid with salt (MILS) sample carried out at different temperatures have revealed the presence of worm like micelles.
- Rheological studies on BmimCl with 18.7 wt% concentrations of LiCl have indicated the presence of large scale association structures which are known to be responsible for the high viscosity of the sample at low temperatures (<80°C) which disintegrate into constituent units at high temperature (>80°C). The weak gel state observed at high temperatures arises due to the disintegration of the association structures at high temperature along with concomitant formation of micellar network structures.
- Silica-ionic liquid nanocomposite (SINC) has been prepared by dispersing different amounts of silica nanoparticles in EmimTFSI ionic liquid. Dynamic rheological studies on SINC samples with different concentrations of silica nanoparticles have been carried out at different temperatures and the elastic modulus of the samples is found to increase upon increasing the temperature.
- SINC samples with lower concentrations of silica nanoparticles (<3 wt%) is found to exhibit a weak gel behavior whereas samples with higher concentrations (>3 wt%) showed a strong gel behavior. This transformation is attributed to the formation of increased number of colloidal networks upon increasing the concentration.
• Rheological studies on SINC samples with lower concentrations of silica nanoparticles (<3wt%) as a function of temperature have shown a strong gel behavior at high temperatures and a weak gel behavior at low temperatures.

# References

[1] U. Gasser, E. R. Weeks, A. Schofield, P. N. Pusey, D. A. Weitz, Science 292 (2001)258.

[2] B. V. R. Tata, S. S. Jena, Solid State Commun 139 (2006) 562

[3] A.K. Sood, Structural ordering in colloidal suspension, in: H. Eherenreich, D. Turnbull (Eds.), Solid State Phys., vol. 45, Academic, New York, 1991, pp. 1–73.

[4] P. N. Pusey, W. V. Megan, Phys. Rev. Lett. 59 (1987) 2083.

[5] B. V. R. Tata in Statistical Physics of Complex Fluids, Eds, S. Maruyama, M. Tokuyama, Tohoku University Press, Sendai, Japan, 2007.

[6] R. S. Crandeall, R. Williams, Science, 198 (1977) 293.

[7] S. J. Farouji, M Atakhorrami, D. Mizuno, E. Eiser, G. H. Wegdem, F. C. MacKintosh, D. Bonn, C. F. Schmidt, Phys. Rev. E 78 (2008) 61402.

[8] H. Tanaka, J. Meunier, D. Bonn, Phys. Rev. E 69 (2004) 31404.

[9] A. D. Biasio, G. Bolle, C. Cametti, P. Codastefeno, F. Sciortino, P. Tartaglia, Phys. Rev. E 50 (2004) 1649.

[10] H. Asai, A. Masuda, M. Kawaguchi, J. Colloid. Interface. Sci., 328 (2008) 180.

[11] R. G. Larson, The Structure and Rheology of Complex Fluids, Oxford University Press, New York, 1999.

[12] Y. W. Mai, Z. Z. Yu, Polymer Nanocomposites, Woodhead Publishing Ltd, Cambrigde, 2006.

[13] Z. Han, A. Fina, Prog. Polym.Sci. 36 (2011) 914.

[14] K. Holmberg, B. Jonsson, B. Kronberg and B. Lindman, Surfactants and Polymers in aqueous solution, John Wiley & Sons Ltd, 2002.

- [15] S. Singh, Liquid Crystal Fundamentals, World Scientific & Publishing Co, 2002.
- [16] R. Bandyopadhyay, A. K. Sood, Langmuir, 19 (2003) 3121.
- [17] N. A. Mazer, G. B. Benedek, M. C. Carey, J. Phys. Chem., 80 (1976) 1075.
- [18] P. A. Hassan, S. R. Raghavan, E. W. Kaler, Langmuir 18 (2002) 2543.
- [19] P. A. Hassan, G. Fritz, E. W. Kaler, J. Colloid. Interface. Sci., 257 (2003) 154.
- [20] W. J. Kim, S. M. Yang, J. Colloid. Interface. Sci., 232 (2000) 225.
- [21] Y. Osada, Y. R. Khokhlov, Polymer gels and networks, Marcel Dekkar. Inc, New York, 2005.
- [22] T. Welton, Chem. Rev 99 (1999) 2071-2084.
- [23] R.P. Swatloski, S.K. Spear, J.D. Holbrey, R.D. Rogers, J. Am. Chem. Soc., 124(2002) 4974-4975.
- [24] H. Xie, S. Zhang, L. Shengai, Green. Chem, 8 (2006) 630-633.
- [25] J.L. Anderson, V. Pine, E.C. Hag berg, V.V. Shears, D.W. Armstrong, Chem. Common, (2003) 2444-2445.
- [26] D. F. Evans, A. Yamauchi, G. J. Wei, V. A. Bloomfield, J. Phys. Chem. 87 (1983)3537.
- [27] N. A. Jose, C. Lopes, A. A. H. Padua, J. Phys. Chem. B, 110 (2006) 3330-3335.
- [28] K. Iwaita, H. Okajima, S. Saha, H. Hamaguchi, Acc. Chem. Res. (2007)401174–1181.
- [29] J. Wu, J. Zhang, X. Zhao, N. Li, B. Dong, Colloids and Surfaces A: Physicochem.Eng. Aspects 336 (2009) 18–22.
- [30] Q. Kuang, J. Zhang, Z. Wang, J. Phys. Chem. B. 114 (2010)15742–15752.
- [31] S. Patra, A. Samanta, J. Phys. Chem. B. 116 (2012)12275–12283.

[32] I. Kilpelainan, H. Xie, A. King, M. Granstorm, S. Heikkenin, S. Argyropolous, J. Agric. Food Chem. 55 (2007)9142–9148.

[33] K. A. Fletcher, S. Pandey, Langmuir, 20 (2004)33-36.

[34] C. R. Lopez-Barron, N. J. Wagner, Langmuir, 28 (2012)12722-122730.

[35] X. Wang, Q. Li, X. Chen, Z. Li, Langmuir, 28 (2012)16547-16554.

[36] S. B. Velaser, M. Turmine, D. D. Caprio, P. Letellier, Colloids and Surfaces A: Physicochem. Eng. Aspects 275 (2006) 50-54.

[37] P. Ghosh, Colloid and Interface Science, PHI Learning (P) Ltd, New Delhi, 2009.

[38] C.W. Macosko, Rheology: Principles, Measurements and Applications, VCH Publishers, New York, 1994.

[39] A. Takada, K. Imaichi, T. Kagawa, Y. Takahashi, J. Phys. Chem. B, 112 (2008)9660–9662.

[40] M.J. Monteno, F.F.C. Bazito, L.J.A. Siqueira, M.C.C. Ribeiro, R.M. Torresi, J.Phys. Chem. B 112 (2007) 2102-2109

[41] K. Ueno, K. Hata, T. Katakabe, M. Kondoh, M. Watanabe, J. Phys. Chem. B, 112(2008) 9013-9019.

### **CHAPTER 2**

### **Experimental Techniques**

This chapter deals with the technical details and experiments used for characterizing the samples using rheology, Small Angle Neutron Scattering (SANS), surface tension measurements and turbidity measurements. Various geometries used for carrying out rheological studies are described. Details of small angle neutron scattering facility at Bhabha Atomic Research Centre (BARC), Trombay used for identifying the worm-like micelles is also described in brief.

### 2.1 Rheology

Rheology is the study of flow and deformation of matter [1]. Flow and deformation are the result of relative movements of particles within the material on the application of external force [2]. The reaction to the external force is dependent on the state of the material. Liquids and gases flow on the application of external force whereas solids deform. Under the application of low stresses, the strain experienced by the solids varies linearly. This linear dependence of stress over strain is called Hooke's law and it is characterized by the proportional constant, called modulus. On the removal of the applied stress, the solids retain their shape since the deformation is elastic. On the otherhand, on the application of stress, the liquids flow and the shear rate linearly varies with the applied stress. This linear dependence of the applied stress over the shear rate is called Newton's law and the proportionality constant is called coefficient of viscosity or viscosity.

For an elastic solid,

$$\sigma = G\gamma \tag{2.1}$$

For a viscous liquid,

$$\sigma = \eta \dot{\gamma} \tag{2.2}$$

where  $\sigma$ , G,  $\gamma$ ,  $\eta$  and  $\dot{\gamma}$  are shear stress, shear modulus, shear strain, viscosity and shear rate respectively.

# 2.1.1 Non- Newtonian behavior

There are many materials which do not obey the above mentioned the laws. Indeed these materials are more in number when compared to the ideal solids and liquids. These materials include polymer solutions, colloidal suspensions, solutions of biological macromolecules, solutions food polysaccharides and hydrocolloids, paints, inks, clay, biological fluids, etc. Viscosity of these materials is dependent on the shear rate applied. They are called non-Newtonian fluids.



Shear rate,  $\dot{\gamma}$ 

# Fig. 2.1 Schematic representation of different types of flow behavior

Two types of rheological tests are commonly employed to probe the flow properties. They are rotational and oscillatory tests. In rotational measurements, a rotational stress/strain is applied and the resulting strain/stress is measured. Rotational measurements are generally used to characterize the given sample is Newtonian or shear thinning or shear thickening behavior as shown in Fig. 2.1. The viscosity of a shear thinning fluid decreases upon increasing the shear rate, whereasfor a shear thickening fluid viscosity increases upon increasing the shear rate. On the other hand, the viscosity of the Newtonian fluid remains constant with respect to shear rate.

# 2.1.2 Linear Rheology

Linear rheology is the study in which sinusoidal strain/stress of angular frequency,  $\omega$  is applied to a material in the linear viscoelastic region and the corresponding phase shifted sinusoidal stress/strain is measured. The magnitude of the applied stress/strain amplitude is very small in such a way that it should not distort the existing structure of the material. Linear viscoelastic region refers to the region where the rheological parameters are invariant with respect to input stress/strain amplitude and depends only on  $\omega$ . Mathematically, complex expressions are convenient and hence they are used here. The applied complex sinusoidal strain,  $\gamma^*$  is expressed as

$$\gamma^* = \gamma_0 \exp\left(i\omega t\right) \tag{2.3}$$

Corresponding shear rate is given by

$$\dot{\gamma}^* = i\gamma_0 \omega \exp\left(i\omega t\right) \tag{2.4}$$

The stress response to the applied  $\gamma$  is given by,

$$\sigma^* = \sigma_0 \exp i[\omega t - \delta(\omega)] \tag{2.5}$$

where  $\gamma_0$  and  $\sigma_o$  are strain and stress amplitudes,  $\omega$  is applied angular frequency and  $\delta$  is phase difference between the applied strain and the measured stress.

The complex modulus  $G^*$  is given by the ratio of complex stress to the complex strain *i.e* 

$$G^* = (\sigma_0^* / \gamma_0^*) = (\sigma_0 / \gamma_0) \exp[i\delta(\omega)] = (\sigma_0 / \gamma_0) [\cos\delta(\omega) + i\sin\delta(\omega)]$$
(2.6)

But,  $G^* = G' + iG''$  where, G' is elastic modulus which measures the strength of the material to store energy and G'' is viscous modulus which measures the strength of the material to dissipate energy. The expressions for G' and G'' are given by from Eq. (2.5),

$$G' = (\sigma_0 / \gamma_0) \cos \delta(\omega) \tag{2.7}$$

$$G'' = (\sigma_0 / \gamma_0) \sin \delta(\omega) \tag{2.8}$$

$$\tan\delta = G''/G' \tag{2.9}$$

where  $\tan \delta$  is called damping factor.

Linear rheological measurements are very important in the rheological characterization of a given material. Using these measurements one can identify whether the given material is viscoelastic liquid or gel or weak gel or an entangled polymer solution. As shown in fig, in the case of gels, G' and G'' show frequency independence and G'>> G'', for viscoelastic liquids,  $G'\alpha\omega^2$  and  $G''\alpha\omega$  [3], for weak gels, G' and G'' show frequency dependence and G'>G'' and for entangled polymer solutions, at lower frequencies, G''>G' and at higher frequencies, G'>G''.



Fig. 2.2 Schematic representation of various types of rheological behavior of complex fluids

# **2.2 Geometries**

# **Cone and Plate Geometry**

The cone and plate geometry is widely used for both linear and non linear rheological measurements for high viscous samples. In this geometry, the sample is sandwidched between the vertically movable upper cone and a fixed bottom plate. The cone rotates on the sample in which speed of rotation is proportional to the shear rate. In order to ensure uniform shear rate the cone angle is kept small of the order of 1 to  $4^{\circ}$  [1]. Our cone and plate geometry has a cone angle of  $1^{\circ}$ , 25 mm diameter and cone truncation at 0.051mm. When the cone of angle  $\alpha$  and radius *R*, is rotated with an angular speed,  $\Omega$ , the sample is sheared in the  $\phi$  direction as shown in Fig 2.3. The distance between the bottom plate and the cone tip is *d*.

(2.10)

The shear rate,  $\dot{\gamma}$  is given by the expression,

$$\dot{\gamma} = \Omega / \tan \alpha$$



Fig. 2.3 Schematic of cone and plate geometry measuring system

Since,  $\alpha$  is very small (< 4°),

$$\dot{\gamma} = \Omega / \alpha$$



Fig. 2.4 Photographs of (a) cone and (b) plate geometry

Hence it is clear from Eq. (2.11) that the shear rate is dependent only on the rotational speed and provides constant shear rate throughout the sample. The corresponding shear stress,  $\sigma$  is given by

$$\sigma = 3M/2\pi R^3 \tag{2.12}$$

Where, M is the applied torque for generating the given stress. The viscosity of the sample is given by the ratio of shear stress and shear rate

$$\eta = 3M\alpha/2\pi R^3 \Omega \tag{2.13}$$

# **Double Gap geometry**

Concentric cylinder geometry, in which the sample is sheared in the gap between the two cylinders, is widely used to measure the rheology of low viscous materials. Double gap geometry as shown in the Fig. 2.5, is a better geometry in which shear area is doubled as compared to the conventional concentric cylinder geometry [4].

(2.11)

It consists of three concentric cylinders in which middle cylinder is allowed to rotate. The sample is placed in such a way that it wets inner and outer part of the middle cylinder as shown in the Fig. 2.5.



Fig. 2.5 Schematic of double gap measuring system



Fig. 2.6 Photograph of double gap geometry

In this geometry there are four radii  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  as shown in the Fig. 2.5 and they are related by the expression [5]

$$\delta = R_2 / R_1 = R_4 / R_3 \le 1.15 \tag{2.14}$$

The expressions for shear rate,  $\dot{\gamma}$ , shear stress,  $\sigma$ , and viscosity,  $\eta$  are given by [5],

$$\dot{\gamma} = \pi n (1 + \delta^2) / 30 (\delta^2 - 1) \tag{2.15}$$

$$\sigma = M(1 + \delta^2) / (4000(\delta^2 R_3^2 + R_2^2)\pi LC_L)$$
(2.16)

$$\eta = (M/400\pi^2 LC_L)(1/\delta^2 R_3^2 + R(e)[3(\delta^2 - 1)/n]$$
(2.17)

where, *M* is the applied torque for generating the given stress, *n* is rotational speed, *L* is the length of the sample under shear and  $C_L$  is the end effect correction factor.

# 2.3 Rheometer and Measurements

Rheological measurements have been carried out using MCR 301 Rheometer (M/s Anton Paar, Germany) with a cone & plate measuring system having a cone angle of  $1^{\circ}$  and diameter of 25mm (for high viscous samples) and double gap measuring



Fig. 2.7 Photograph of Rheometer system (a) Air compressor, (b) Movable rheometer head, (c) Rheometer (MCR 301) (d) Counter cooling system and (e) Anti vibration Table

system (for low viscous samples). The rheometer setup (Fig. 2.7) consists of air compressor for providing the air bearing for vertical movement of the rheometer head, rheometer, counter cooling system for cooling the Peltier system and an anti-vibration table. This rheometer can be operated both in controlled stress as well as controlled strain mode. However, all rheological measurements presented in this thesis has been carried out in controlled strain mode. It has a torque range of 0.1µNm-200 mNm with a resolution of  $0.001\mu$ Nm. The applied frequency range is  $10^{-4}$ -100 Hz. The maximum accessible shear stress and shear rate are 49,000 Pa and 17,520 s<sup>-1</sup> for cone/plate geometry and 2190 Pa and 9250 s<sup>-1</sup> for double gap geometry. The sample temperature is varied using a Peltier unit with hood and is maintained to an accuracy of  $\pm 0.01$  °C. The minimum and maximum temperatures for this rheometer are -10°C and 200°C. Frequency sweep measurements have been performed in the frequency range of 0.1 -100 rad/s in the linear viscoelastic region. A linear viscoelastic region is a region where the rheological parameters like G', G'' etc are independent of the applied strain/stress amplitude. Experimentally, this region is the plateau region in a strain sweep measurement where the parameters are constant as a function of strain amplitude. Flow measurements have been carried out in the range  $0.01 - 1000 \text{ s}^{-1}$  for all the samples. While performing the experiments in order to avoid moisture absorption, the outer width of the sample exposed to atmosphere was covered by a thin layer of low viscosity silicone oil.

# 2.4. Small angle neutron scattering

Small angle neutron scattering (SANS) is basically a diffraction experiment where thermal neutrons are used to probe the colloidal structures at small scattering angles. The wavelengths of these neutrons are generally in the range of 4 to 10 Å. The

scattering centres for these neutrons are nuclei of the sample where each nucleus is characterized by an effective scattering length. Since, the wavelengths of thermal neutrons are very high compared to the nuclear size, each nucleus acts as a point scatterer. Neutrons interact with the magnetic moment of the nucleus and hence the scattering intensity depends of the state of nuclear spin which leads to coherent and incoherent scattering. The incoherent scattering is an unwanted noise which is independent of the scattering wave vector, q. The q dependent coherent scattering is extracted from the scattering data by subtracting the incoherent background. The SANS intensity, I(q) from dilute colloidal particles dispersed in a solvent consists of three distinct regions namely, the low q Guiner region, intermediate q region and high qPorod region as shown in the Fig 2.8 where ln I is plotted against ln q.

When  $q \ll 1/R_g$ , where,  $R_g$  is the radius of gyration of the particle, the scattered intensity is weakly dependent of q and is independent of the shape of the particle. In the Guiner region, the scattering intensity is expressed as

$$I(q) = I(0) \exp(-q^2 R_q^2/3)$$
(2.18)

where, I(0) is the intensity at q=0

At higher q values, the scattering intensity varies as  $q^{-n}$  when  $q >> 1/R_g$ . The exponent on q, n = 4, for smooth surfaces, 3 < n < 4, for surface fractals and 1 < n < 3 for mass fractals. This high q region is called Porod region. In this high q values, scattering from the surface of the particle is effective and one can estimate the surface area of the particle. In the intermediate region i.e.  $q \sim 1/R_g$ , from the value of slope, one can estimate the shape of the particle. For example, the scattering intensity from cylindrical and disc like particles has slopes one and two respectively in the intermediate q region.



Fig. 2.8 Various regions in SANS scattering profile

SANS measurement has been widely used to estimate the size and shape of the wormlike micelles [8]. The scattered intensity from the worm-like micellar solutions varies as  $q^{-1}$  and in the double logarithmic plot (*lnIvslnq*), the slope of curve is equal to -1 [6, 7]. Hence, by measuring the slope of the scattering curve, one can identify the presence of wormlike micelles.

### Scattering intensity and structure factors

In SANS one measures the scattered intensity from the given sample as a function of q and expressed as

$$I(q) = KT_s t d\Sigma(q) / d\Omega \tag{2.19}$$

where *t* is the sample thickness,  $T_s$  is the sample transmission and *K* is a constant depends on the instrument parameters like incident neutron flux, detector efficiency, solid angle etc. and  $d\Sigma(q)/d\Omega$ , macroscopic differential cross section due to scattering by the particles present in the solution. Since, *t*,  $T_s$ , and *K* are independent of *q*, the scattered intensity as a function q, is directly proportional to the differential cross section,  $d\Sigma(q)/d\Omega$ .

In the case of scattering by monodisperse colloidal particles, the differential cross section is given by

$$d\Sigma(q)/d\Omega = n(\rho_p - \rho_s)^2 V^2 P(q) S(q)$$
(2.20)

Where, *n* is the number density of the particles,  $\rho_p$  and  $\rho_s$  are scattering length densities of particles and solvent, *V* is the volume of the particle, P(q) is the intraparticle structure factor and S(q) is the interparticle structure factor. The term,  $(\rho_p - \rho_s)^2$  is defined as contrast factor and determines the scattering contrast between the particle and the solvent. The scattering length of hydrogen is negative (-0.37 × 10<sup>-12</sup> cm) whereas for deuterium is positive (0.67 × 10<sup>-12</sup> cm) [8]. This gives an advantage that deuterating the hydrogen atoms of either solvent or particle increases the contrast factor and improves the scattering profile. In the case of dilute particles, *S*(*q*) becomes unity and hence the scattering cross section depends fully on *P*(*q*) and expressed as

$$d\Sigma(q)/d\Omega = n(\rho_p - \rho_s)^2 V^2 P(q)$$
(2.21)

# Intraparticle structure factor

Colloidal particles having well defined shapes like spheres, cylinders etc., have intraparticle structure factors with analytical expressions. A random orientation of the particles is assumed. In the case of spherical particle with radius, R', the interparticle structure factor is given by

$$P(q) = [3(\sin(qR') - qR'\cos(qR'))/(qR')^3]^2$$
(2.22)

# **Experimental setup**

The SANS experiments are carried out using the setup at Dhurva reactor, BARC, Trombay [7]. The block diagram of the experimental setup of SANS is shown in Fig. 2.9. Neutrons of different wavelengths from the source are allowed to pass through a monochromator which consists of polycrystalline BeO filter kept at liquid nitrogen temperature. The monochromator allow only wavelengths above 4.7 Å while other wavelengths are Bragg reflected. The mean wavelength of the neutrons is 5.2 Å. After the monochromator, the neutron beam is collimated by two slits separated by a distance 2 m.





Liquid samples in quartz sample holders are mounted on a square (10 cm  $\times$  10 cm) sample table. The scattered neutrons from the sample are collected by a position sensitive detector which is kept at distance of 1.85 m from the sample. The detector is positioned in such a way that it will allow neutrons scattered between the angles, 1 to  $15^{\circ}$  or a *q* range of 0.018 to 0.32 Å<sup>-1</sup> [7, 8].

# 2.5 Surface Tension

A Wilhelmy plate method has been used to measure surface tension using Sigma 703 digital surface tensiometer. The surface tension is measured with an accuracy is 0.1 mN/m. This method consists of a thin platinum plate and a Teflon vessel for carrying the solution whose surface tension to be measured. The maximum weight of the sample is 5 gram. The platinum plate is dipped in the given solution and pulled slowly away from the solution and the corresponding force is monitored. The maximum force is recorded during the detachment of the plate from the surface of the solution since the contact angle becomes  $0^{\circ}$ .



Fig. 2.10 Illustration of Wilhelmy plate method for measuring surface tension

The surface tension, S is given by the expression

$$S = F/P\cos\theta \tag{2.23}$$

Where *F* is the force experienced by the plate and *P* is the perimeter of the plate

When  $\theta = 0^{\circ}$ , then the expression for surface tension is reduced to

$$S = F/P \tag{2.24}$$

### 2.6 Visible spectrophotometer

Turbidity measurements have been carried out using HACH DR 2800 visible spectrophotometer at 600 nm. The spectrophotometer uses gas filled tungsten lamp as source with a wavelength range of 340 nm to 900 nm. The wavelength resolution is 1 nm. The sample is sandwiched between two quartz plates having a groove (optical path length, L) of depth 0.2 mm. The loaded cell was heated to the required temperature in the HACH COD digester for half an hour and transferred immediately to spectrophotometer and measured the intensity.





Turbidity  $(\tau)$  is estimated according to the formula,

$$\tau = (-1/L) ln(I_t/I_o)$$
(2.25)

Here,  $I_t$  is the transmitted light intensity of the sample; and  $I_o$  is the incident light intensity.

# References

[1] T. A. Mazder, Rheology Handbook, Vincentz Network GmbH & Co, K.G.

[2] C.W. Macosko, Rheology: Principles, Measurements and Applications, VCH Publishers, New York, 1994.

[3] R. G. Larson, The Structure and Rheology of Complex Fluids, Oxford University Press, New York, 1999.

[4] J. W. Goodwin, R. W. Hughes, Rheology for Chemists, Royal society for chemistry, 2000.

[5] Anton Paar Manual for MCR 301 Rheometer, 2006.

[6] L. Brinchi, R. Germani, P. D. Profio, L. Marte, G. Savelli, R. Oda, D. Berti, J.Colloid Interface Sci 346 (2010) 100-106

[7] V. K. Aswal, P. S. Goyal, Pramana J. Physics, 63 (2004) 65-72.

[8] V. K. Aswal, P. S. Goyal, Curr.Sci, 79 (2000) 947-53.

# CHAPTER 3

# Rheological Studies and Surface Active Properties of BmimCl and its Aqueous Solutions

## **3.1 Introduction**

BmimCl ionic liquid is hygroscopic, hydrophilic and solid at room temperature. However, the supercooled form of this IL remains as liquid at room temperature [1]. It is miscible in water at all concentrations. It is a protic IL from which other ILs of Bmimcation like BmimBF<sub>4</sub>, BmimPF<sub>6</sub>, Bmim TFSI etc. are derived. X-ray diffraction studies have revealed two crystal structures of Bmimcation, namely orthorhombic and monoclinic [2]. Raman spectroscopy studies on BmimCl have revealed the presence of coexistence of two rotational isomers namely, trans and gauche [2]. Similar to other ILs as discussed in chapter 1, BmimCl possess local association structures. Kuang*et al* have studied BmimCl at different temperatures ranging from supercooled state to liquid state using dynamic light scattering (DLS) and found the presence of local heterogeneities with long persistence lengths (100-400 nm) [3]. These heterogeneities are formed by long range density fluctuations due to the strong hydrogen bonding between cations and anions and aggregation of alkyl chains of cations. However, there are no rheological studies on BmimCl in connection with its local structures.

The next chapter deals with SDS micellar solutions prepared in BmimCl. We characterize BmimCl ionic liquid for the rheological behavior at room temperature as well as at elevated temperatures and the results are reported here. Since BmimCl is hygroscopic, it is of interest to know how the presence of water influences the flow properties and rheological behavior. Towards this we have carried out detailed rheological investigations in aqueous BmimCl solutions and the results are reported here. Many ionic liquids possess surface active properties when dissolved in water and

forms micelles like conventional surfactants [4]. The presence of alkyl chain in the cation of ILs is responsible for the surface active behavior [4, 5].

Motivated by the above studies, we have carried out dynamic rheological measurements at different temperatures for BmimCl and surface tension measurements and flow measurements for aqueous BmimCl solutions as a function of BmimCl concentration and the results are presented in this chapter.

# 3.2 Materials and methods

Rheological measurements on BmimCl samples have been carried out using MCR 301 Rheometer (M/s Anton Paar, Germany) with a cone & plate measuring system having a cone angle of 1° and diameter of 25mm. The sample was dried under Argon atmosphere in the measurement position about 2.5 hrs on the rheometer plate at 126°C prior to the measurements. The outer width of the sample exposed to atmosphere was covered by a thin layer of low viscosity silicone oil to avoid moisture absorption. and double gap geometry for aqueous BmimCl solutions. Each sample is equilibrated for 10 min at each temperature. For aqueous BmimCl solutions, double gap geometry was used with an equilibration time 15 min. Surface tension measurements using Sigma 703 digital surface tensiometer the details of these instruments are detailed in chapter 2.

### 3.2.1 Synthesis of BmimCl

BmimCl is synthesized by refluxing the mixture of 1-metylimidazole and butyl chloride. Before synthesis, 1-metlylimidazole is purified through distillation. 1-metylimidazole and butyl chloride are mixed in a round bottomed flask in the ratio 1:1.2 and stirred at 70°C for 72 hours [1, 2].

1-methylimidazole (liq) + butylchloride(liq)

*Reflux, 70°C BmimCl*<sub>(solid)</sub> *72 hours*  The resulting product is washed several times with ethyl acetate and acetonitrile and evaporated under vacuum at 343 K. A white solid is obtained after cooling. The moisture content is minimized (<0.6 wt %) by vacuum drying at 80°C for 12 hrs.

# 3.2.2 Estimation of water content using Karl-Fisher Titration

Since BmimCl samples are highly hygroscopic and the water (moisture) content in BmimCl has to be estimate, before it is used as a solvent for preparing different concentrations of Micellar-ionic liquid sample. In order to estimate the water content in the BmimCl ionic liquid, Karl Fisher Titration method has been used and the procedure is described below.

Karl Fisher Titration method is basically a coulometric titration method which is used to measure trace amounts of moisture present in a given sample. The titration cell consists of methanol as the solvent medium in which a known small quantity of the sample is titrated against Karl Fisher reagent (KFR). The cell is made free from atmospheric moisture by sealing its mouth with molecular sieves. First, a known weight of water is titrated with KFR and the quantity of KFR required to neutralize the water is noted. This process is repeated for atleast three times and the average of these values is termed as KFR equivalent (*KFR<sub>eq</sub>*). Then a small quantity of the sample (~ 1 mg) of known weight is titrated with KFR and the end point is noted. This process is repeated for atleast three times and the quantity of Karl Fisher reagent required to reach the point is termed as KFR consumed (*KFR<sub>con</sub>*) The amount of moisture present in the sample is given by,

% of Moisture = 
$$[KFR_{con}(ml) \times KFR_{ea}(mg/ml) \times 100]/sampleweight(mg)$$
 (3.1)

# 3.3. Results and discussion

# **3.3.1 Rheological studies on BmimCl**

Fig. 3.1 shows the frequency sweep measurements of BmimCl at six different temperatures. Upto  $60^{\circ}$ C, the IL exhibits a liquid like behavior as G'' is always greater



Fig. 3.1 *G'* (closed circles) and *G''* (open circles) as a function of  $\omega$  forBmimCl at different temperatures. The lines on *G'* and *G''* data represent the power law fit  $(G'\alpha\omega^2 \& G''\alpha \omega)$ .

than G' in the measured frequency range. Except at lower frequencies, both G'' and G' show power law dependence on  $\omega$  *i.e.* G' $\alpha \omega^2$  and G'' $\alpha \omega$  [6] respectively which is

shown in Fig. 3.1. Crossover of G' over G'' is observed at a frequency of ~70 rad/s, 20 rad/s and 7 rad/s at 80°C, 100°C and 120°C respectively. The frequency at which crossover of G' over G'' occurs, decreases for BmimCl upon increasing the temperature which means the elastic region increases upon increasing the temperature. The presence of non-zero G' at higher temperatures (> 80°C) suggests the presence of local structures and is consistent with the observations by Kuang*et al* [3] as discussed earlier. However they have observed an exponential decay of size of the dynamic networks beyond the melting point of BmimCl. But our rheological studies do not show any decrease of G'beyond the melting point. This may be attributed to the association of local heterogeneities of BmimCl molecules under shear.

To get a deeper insight, flow measurements are carried out on BmimCl at different temperatures and the results are presented in Fig. 3.2 (closed symbols). At lower temperatures ( $<60^{\circ}$ C), the viscosity is independent of shear rate *i.e.* Newtonian behavior is observed. However, a small shear thinning starts to develop at lower shear rates ( $\geq 60^{\circ}$ C) which increases upon increasing the temperature. At 80°C, the shear thinning region is visible and it continues upto 120°C as shown in the Fig. 3.2. However, the viscosity decreased continuously upon increasing the temperature in addition to the shear thinning behavior.

As discussed earlier, this may be due to the presence of local structures at high temperatures. In order to identify the rheological state of BmimCl at high temperatures, Cox-Merz rule is invoked. Cox-Merz rule, which states that magnitude of the steady shear viscosity  $\eta$  ( $\dot{\gamma}$ ) and complex dynamic viscosity  $\eta^*(\omega)$  superimpose equally at equivalent values of shear rate ( $\dot{\gamma}$ ) and frequency ( $\omega$ ). Generally, Cox-Merz rule holds good for polymer systems like dilute, semi-dilute polymer solutions,

homopolymermelts etc. and in general it is applicable to homogenous systems [7]. Deviation from this rule is observed for heterogeneous systems having crosslinked structures or aggregate structures [8]. Fig. 3.2 (a) shows viscosity of BmimCl samples as a function of shear rate and frequency at 25°C, 40°C, 60°C and 80°C. Upto 80°C, BmimCl obeys Cox-Merz rule as the shear viscosity matches well with the complex viscosity though deviations have been observed at high shear rates at 80°C. This suggests that same molecular arrangements might have occurred [9] in BmimCl under rotational shear and oscillational shear upto 80°C.



Fig. 3.2 Cox-Merz plot of shear viscosity (closed symbols) and complex viscosity (open symbols) as function of  $\omega$  and  $\dot{\gamma}$  at different temperatures.

However, at 100°C and 120°C, complete failure of Cox-Merz rule is observed as shown in Fig. 3.2 (b). At low frequencies and shear rates, shear viscosity is greater than the complex viscosity which suggests the aggregation behavior under flow [10, 11]. However, at high frequencies and shear rates, complex viscosity is greater than shear viscosity which is attributed to the destruction of structures under high shear [12].

Failure of this rule is a characteristic feature of "structured liquids" and "weak gels" [13]. The possibility of weak gels can be ruled out due to the absence of yield stress. Structured liquid is a viscoelastic liquid which does not obey Cox-Merz rule [14]. Hence, at low temperatures, BmimCl exhibits viscoelastic liquid state whereas it behaves like a structured liquid at high temperatures.





Fig. 3.3Surface tension of aqueous BmimCl solutions as a function of BmimCl concentration at 25°C.

Having characterized pure BmimCl rheologically, it is important to check the properties of this IL in water. Studies on aqueous solutions of ILs indicated the ability of these ILs to reduce the surface tension of water (surface activity). In order to know the surface activity of BmimCl, we have carried out surface tension studies on aqueous solutions with different concentrations of BmimCl. Fig. 3.3 shows the surface tension of aqueous BmimCl as a function of concentration of BmimCl at room temperature. The surface tension of the solution decreases upon increasing the concentration of BmimCl. However, we have not observed a saturation of surface tension at high concentrations though we have nearly approched to pure BmimCl. This indicates the absence of micelle formation of BmimCl in water which is attributed to the short alkyl chains (butyl) of the BmimCl cation.

Fig. 3.4 shows the shear viscosity of aqueous BmimCl solutions as a function BmimCl concentration. At lower concentrations (< 5mM), the viscosity is very low (< 10 mPa s) but increases drastically at high concentrations.



Fig. 3 4 Shear viscosity of aqueous BmimCl solution as a function of BmimCl concentration at 25°C. Lines are guide to the eye.

# **3.4 Conclusions**

The ionic liquid BmimCl has been synthesized and dynamic rheological measurements have been carried out at different temperatures. We have checked the validity of Cox-Merz rule and found that BmimCl obeys Cox-Merz rule upto a temperature of 80°C. From this we conclude that, at temperatures beyond 80°C, BmimCl behaves as a structured fluid. Surface tension measurements on aqueous solutions of BmimCl have revealed the surface active property of the IL. However, micelle formation is not favored in water. Flow measurements on aqueous BmimCl solutions suggest that viscosity of the solution increases drastically at higher ionic liquid concentration.

# References

[1] A. Takada, K. Imaichi, T. Kagawa, J. Phys. Chem. B, 112 (2008) 9660.

[2] H. Hamaguchi, R. Ozawa, Structures of Ionic liquids and Ionic liquid compounds:S. A. Rice (ed.), Advances in Chemical Physics, Vol 131, 2005, John Wiley & Sons.

[3] Q. Kuang, J. Zhang, Z. Whang J. Phys. Chem. B, 111 (2007) 9858

[4] P. D. Galgano, O. A. E. Seoud, J. Colloid Interface Sci 361 (2011) 186.

[5]B. Dong, J. Zhang, L. Zheng, S. Wang, X. Li, T. Inoue, J. Colloid Interface Sci 319 (2008) 338.

[6] R. G. Larson, The Structure and Rheology of Complex Fluids, Oxford University Press, New York, 1999.

[7] V. Ojijo, S. S. Ray, Poly (Butylene Succinate) and Poly [(Butylene Succinate)-coadipate] Nanocomposites: L. Averous, E. Pollet (eds.), Environmental silicate Nano-Biocomposites, Springer-Verlog, London, 2012.

[8] J. Lefebre, J. Doubler in Polysaccharides: Structural diversity and functionalversality, edited by S. Dumitriu, Marcel Dekkar, Inc, 1998.

[9]E. E. G., Cruz, J. R. Ramirez, L. L. M. Lagunas, L. M. Torres, Carbohydr. Polym.91 (2003) 394.

[10] S. Y. Chun, B. Yoo, Journal of Food Engineering, 65 (2004) 363.

[11] J. A. L. Silva, M. P. Gonclaves, M. A. Rao, Journal of Food Engineering, 18 (1993) 211.

[12] M. Grassi, R. Lapasin, S. Pricl, Carbohydr. Polym. 29 (1996) 169.

[13] R. Ndjouenkeu, J.O. Akingbala, R.K. Richardson, E.R. Morris, Food Hydrocolloids, 9 (1995) 165.

[14] J. Ahemed, Rheological properties of food: M. M. Farid (ed), Mathematical modeling of food processing, CRC Press, Boca Raton, 2010

### **CHAPTER 4**

# **Rheological Studies on Micellar Ionic Liquid with Salt as a Function Temperature**

# 4.1 Introduction

Micelles are self organized surfactant molecules in a solvent beyond a certain surfactant concentration called critical micelle concentration (CMC). At CMC, micelles are spherical in shape and grow to rod-like shape upon increasing the salt concentration / surfactant concentration [1]. Beyond the persistence length, these rods become flexible (worm-like) and behave like polymer chains. At sufficient concentrations of surfactant, salt and temperature, these semi-flexible cylindrical micelles undergo entanglement and form viscoelastic gel phase. The linear and non-linear rheology of the viscoelastic gel phase of aqueous surfactant solutions have been studied extensively [2]. Surfactants are known to form micelles not only in aqueous medium but also in non aqueous polar solvents [3].

Recently Anderson *et al* [4] have reported the formation of large size SDS micelles in an ionic liquid, BmimCl (1-butyl 3-methylimidazolium chloride) beyond a CMC of ~ 48mM. However they could not measure the size and shape either by light scattering or small-angle-neutron scattering (SANS) techniques due to large amount of scattering leading to the saturation of detectors [4]. Takada *et al* [5] have performed rheology experiments on BmimCl containing different concentrations of LiCl and observed abnormal increase in viscosity and shear thinning behavior at high shear rates. Shear thinning behavior is attributed to the existence of associative structures in BmimCl which undergoes change at high shear rates. The abnormal increase in viscosity is believed to arise from changes in the number and/or size of the large-scale association structure in BmimCl in the presence of LiCl [5-7]. However, there are no

reports on the rheological behavior of BmimCl when LiCl and SDS are present. Further, the effect of temperature on the associative structures present in BmimCl is also not well studied. This chapter reports the rheological study of BmimCl-SDS solution containing different concentrations of LiCl salt (4.8, 9, 13.1 & 18.7 wt%) *i.e.* ionic liquid with salt (MILS) a as a function of temperature (T).

# 4.2 Materials and methods

BmimCl was synthesized as reported elsewhere [8] and the moisture content was minimized (<0.6 wt %) by vacuum drying at 80°C for half a day. SDS (98%, Acros Organics), LiCl (Anhydrous, 99.99%, Sigma Aldrich) and deuterated SDS (98%, D25 Cambridge isotope laboratory) were used as received.

# 4.2.1 Sample preparation

Micellar ionic liquid samples with different amounts of LiCl for a given concentration of SDS are prepared. 200mM SDS (4.45 wt%) in BmimCl is prepared by mixing required amounts of SDS and BmimCl in a round bottom flask, hermetically sealed immediately and the mixture is stirred for 45 minutes at 90°C to obtain a homogenous turbid solution of micellar ionic liquid (MIL). To this, different amounts of LiCl is added and stirred for about 12h at 120°C to get a homogenous solution of MIL sample with LiCl concentrations as mentioned in Table 4.1 (MILS sample). MILS sample with deutriated SDS and 4.45 wt% deutriated SDS in BmimCl are prepared in the same way as mentioned above for carrying out small angle neutron scattering (SANS) experiments.

Rheological measurements on MILS sample have been carried out using MCR 301 Rheometer (M/s Anton Paar, Germany) with a cone & plate measuring system

having a cone angle of 1° and diameter of 25mm. The sample was dried under Argon atmosphere in the measurement position about 2.5 hrs on the rheometer plate at 126°C prior to the measurements. The outer width of the sample exposed to atmosphere was covered by a thin layer of low viscosity silicone oil to avoid moisture absorption. The sample temperature is varied using a Peltier unit with hood and is maintained to an accuracy of  $\pm 0.01^{\circ}$ C. The storage and loss moduli  $G'(\omega)$  and  $G''(\omega)$ , of the sample were measured using a frequency sweep of 0.1 - 100 rad/s at five different temperatures, 40°C, 60°C, 80°C, 100°C and 120°C. Samples are equilibrated for 15 minutes at each temperature. For experimental details of rheometer, SANS and turbidity measurements refer chapter 2.

Concentration of LiCl (wt%) in		
Micellar Ionic liquid	State ( $T = 40^{\circ}$ C - 120 <sup>o</sup> C)	
4.8	Viscoelastic liquid	
9	Viscoelastic liquid	
13.1	Viscoelastic liquid	
18.7	Viscoelastic liquid ( <i>T</i> <80°C) Weak gel ( <i>T</i> >80°C)	
21.1	Salt did not dissolve	

Table.4.1

State of the MILS	<b>S</b> sample having	different concentrations	of LiCl
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# 4.3 Results and discussion

### 4.3.1 Viscoelastic liquid and weak gel states of MILS sample

In order to identify the linear viscoelastic region of the MILS having 18.7 wt% LiCl at different temperatures, strain sweep measurements have been carried out at sufficiently low  $\omega$ =5rad/s. The strain response is found to be linear up to  $\gamma_0 \le 1\%$  for all temperatures by measuring the complex viscosity,  $\eta^*(\omega)$  as a function of strain amplitude. All measurements were performed within the linear viscoelastic region. Frequency dependent G' and G'' of MILS sample were measured in the frequency,  $\omega$ range between 0.1 and 100 rad/s at controlled constant temperatures. Fig.4.1 shows the plots of G'and G'' as function of  $\omega$ at five different temperatures. Notice that at 40°C, (Fig. 4.1A) G'' is higher than G' throughout the measured frequency range  $\omega$  and the sample slowly flowed upon tilting upside down (top picture in Fig.4.2). When the sample is heated to 60°C, a crossover of G' is observed at  $\omega \sim 0.25$  rad s<sup>-1</sup> (Fig.4. 1C) and the  $\omega$  at which this crossover occurs is found to increase with increase in temperature (Fig.4.1D & E). At 120°C the G' is found to be higher than G'' (Fig. 4.1B) in the entire of  $\omega$  region. Further, notice from Fig.4.1 that the difference between G' and G'' is not high (damping factor,  $\tan \delta = G''/G' \sim 0.6$ ) and exhibits  $\omega$  dependence unlike for a gel (usually tan $\delta < 0.01$ , G' is independent of  $\omega$ ). These observations suggest a sol-gel transition occurring in MILS sample upon increasing the temperature from Fig. 4.1B that the difference between G' and G'' is not high (damping factor, tan $\delta$ =  $G''/G' \sim 0.6$ ) and exhibits  $\omega$ dependence unlike for a gel (usually tan $\delta < 0.01$ , G' is independent of  $\omega$ ). These observations suggest that the sample exhibits weak gel behavior for  $T \ge 80^{\circ}$ C [8]. The storage modulus G' and loss modulus G'' also showed power law behavior (Fig. 4.1B) similar to that reported in weak gel [9] and gel systems [10]. It can be seen from Fig (4.1B & E) G' is relatively independent of  $\omega$ (over two decades of dynamic range at low  $\omega$ ) showing the gel characteristics of MILS sample at high temperatures. Observations suggest a solution to gel transformation occurs in MILS sample upon increasing the temperature. Similar high temperature gelation is also observed in ionic liquids with the addition of triblock copolymers [11].



Fig. 4.1 *G'* (closed circles) &*G''* (open circles) for the MILS sample having 18.7 wt% LiCl as a function of frequency,  $\omega$  at different temperatures.

In order to identify unambiguously the viscoelastic liquid and weak gel state in MILS sample, we have carried out dynamic strain sweep measurements and G', G'' plots as a function of  $\gamma_o$  measured at different temperatures are shown in Fig.4. 2.

Notice that at temperatures 40°C and 60°C (Fig.4. 2A) *G'* does not cross *G"*whereas at 100°C and 120°C (Fig. 4.2B) *G'* crosses *G"* at a value of  $\gamma_o$  (%) = 2.5 and 11.7 respectively. The  $\gamma_o$  value at which the cross over occurs is defined as yield strain [12, 13]. The yield stress values corresponding to the yield strain values at 100 and 120°C are 0.4 and 0.6 Pa, respectively. Though MILS sample at 80°C (Fig.4.1D) exhibited *G'>G"*at low  $\omega$  region, we could not measure a reliable yield stress value using our rheometer at such low  $\omega$ (<1 rad/s). Thus it is clear from Fig.4.1 and 2 that at low temperatures, the MILS sample is viscoelastic liquid which undergoes transition to a weak gel state beyond 80°C. Notice in Fig. 4.2B that *G'* and *G"* show a monotonic



Fig. 4.2 A G' (closed symbols) & G'' (open symbols) as a function of strain amplitude at different temperatures at A: 40 and 60°C and B: 100 and 120°C. Dotted lines indicate the yield strains at 100°C and 120°C. Pictures of the MILS sample at 40°C and 120°C. Top picture is taken five minutes after the sample is kept upside down and a shows weak flow. Bottom picture is taken immediately after the sample is kept upside down.

decrease with increase in  $\gamma_{o.}$  Similar monotonic decrease was also observed in other soft matter systems exhibiting weak gel and gel behavior [14, 15]. However, there are also weak gels and other soft matter systems which exhibit a continuous decrease of *G*'but a distinct peak in *G*"above a critical strain [16-18]. So, a distinct peak in *G*"is not a characteristic of all weak gels.

# 4.3.2 Viscoelastic behavior of MILS samples with lower concentrations of LiCl

With an aim to observe a weak gel state at another concentration of LiCl, we have prepared four more samples of MILS with three lower concentrations of LiCl (i.e.
4.8, 9.0, 13.1 wt%) and one having a higher concentration of 21.1 wt% of LiCl, while keeping the SDS concentration fixed at 4.45 wt%. At 21.1 wt%, the LiCl could not be dissolved completely; hence we did not proceed with the rheological studies. We carried out oscillatory and strain sweep measurements over a temperature range of 40 to 120°C on MIL samples with 4.8, 9.0 and 13.1 wt% LiCl. The MILS samples with 4.8 and 9.0 wt% LiCl is identified to be in viscoelastic state as their G'' values are found to be higher than G'in the entire measured range of  $\omega$ . In the case of sample with 13.1 wt% LiCl, we observed G' < G'' up to 80°C and G' > G'' in the low  $\omega$ region (Fig. 4.3) but no reliable yield stress value could be measured for the reason mentioned above. The rheological characterization of the state of MILS samples with different concentration of LiCl is summarized in Table. 4.1.



Fig. 4.3 G' (closed circles) & G'' (open circles) as a function of frequency,  $\omega$  for BmimCl sample with 13.1 wt% LiCl, 4.45 wt% SDS at two different temperatures A: 80°C and B: 100°C.

#### 4.3.3 Presence of Worm-like micelles in MILS sample

The weak gel state observed at high temperature in MILS sample could be due to the formation of micellar network structures or due to the aggregation of micelles. Which of the two mechanisms responsible for the observed weak-gel behavior can be resolved by performing SANS measurements and investigating the scattering profile (*i.e.* I(q) vs. q) on MILS sample. We have carried out SANS measurements on MILS sample with deutriated SDS and also on a sample with 4.45 wt% deutriated SDS in BmimCl without salt. However, we could not use deutriated BmimCl. The scattering profiles (I(q) vs. q) for these samples are shown in Fig.4. 4. Notice that in 4.45 wt% deutriated SDS in BmimCl sample, the scattering profile is featureless with low scattering intensity and arises entirely due to the incoherent scattering from BmimCl.



Fig. 4.4 SANS data (•) for MILS sample with deutriated SDS and (°) BmimCl sample 4.45 wt% deutriated SDS.

Even though SDS micelles are known to be present [5], they could not be observed as their scattering is buried under the incoherent scattering from BmimCl. The scattering intensity (Fig. 4.4) at large-q from MILS sample with deutriated SDS is featureless and

overlaps with that of 4.45wt% deutriated SDS in BmimCl sample, hence it is attributed to incoherent scattering from the sample. However, the SANS profile shows a strong scattering at low-*q* region and is proportional to  $q^{-m}$  with an exponent value m = 1. It is known from the SANS experiments that worm-like cylindrical micelles show similar scattering profiles with m = 1 [19]. An *m* value of 1.5 to 2 is expected had then been aggregation of micelles in MILS sample [20]. Thus the steep rise in I(q) at low-*q* region of the SANS profile constitutes a clear evidence for the existence of cylindrical form of worm-like micelles in MILS sample at 80°C. We observed similar scattering profiles (not shown) at 40 and 60°C. However, we could not measure SANS profiles in the weak-gel regime (>80°C) due to limitations in the diffractometer set-up.

#### **4.2.4** Presence of network structures in MILS sample

These cylindrical micelles form micellar network structure in MILS sample upon increasing the temperature and is evidenced by the flow curves which are shown in Fig. 4.5. Notice that the sample behaves as a Newtonian fluid up to a temperature  $<80^{\circ}$ C (Fig.4.5) and develops two characteristic regions when the temperature is raised beyond  $80^{\circ}$ C. The region corresponding to low shear rates (see the curves corresponding to 100 and 120°C in Fig. 4.5) exhibits shear thinning whereas the region at high shear rates shows Newtonian behavior. The shear thinning region is found to increase with increase in temperature. The power law decrease with a slope close to -1 at low shear rates implies existence of network structure having yield stress [21, 22]. We have shown in see Fig. 4.2B that in the weak gel state the sample has yield stress. If the applied force exceeds the yield stress, the network structure in gel state is destroyed and the sample flows. Further, we compared the magnitude of the complex dynamic viscosity  $|\eta^*(\omega)|$  and the steady shear viscosity  $\eta(\dot{\gamma})$  at equivalent values of shear rate ( $\dot{\gamma}$ ) and frequency ( $\omega$ ), and found no superposition (i.e. departure from Cox-Merz rule

[23, 24]) in the weak gel state indicating that the networks survive low amplitude oscillatory deformation but may be ruptured by large deformation.



Fig. 4.5 Shear viscosity  $(\eta)$  as a function of shear rate  $(\dot{\gamma})$  at different temperatures for MILS sample.

In the absence of much literature on Ionic-liquid-LiCl-SDS system, it is rather difficult to propose a mechanism for the formation of micellar networks in MILS upon increasing the temperature. However the above mentioned observations *viz.*, (i) SANS studies showing existence of cylindrical worm-like micelles (ii) weak gel state having finite yield stress and (iii) power law decrease of  $\eta$  as a function of  $\dot{\gamma}$  with a slope close to -1 at low shear rates, constitute sufficient evidences for the existence of micellar network structures which we believe are responsible for the weak-gel behavior of MILS sample observed at high temperatures.

#### 4.3.5 Identification of Viscoelastic to Weak gel Transition Temperature



Fig. 4.6 A: Magnitude of complex modulus,  $G^*$  and B: Turbidity vs temperature for the MILS sample. Lines are guide to the eye. Dashed line represents the sol-gel transition temperature at (80°C).

Having characterized the viscoelastic and weak gel state at low and high temperatures respectively, it is important to identify the transition temperature at which MILS sample undergoes transition. Towards this, we performed turbidity and temperature sweep rheological measurements on the MILS sample which are as shown in Fig. 4.6 and Fig. 4.7 respectively. It can be seen from Fig. 4.6A that the magnitude of the complex modulus  $G^*(\omega)$ , decreases with a change in slope at 80°C. However

turbidity ( $\tau$ ), shows a gradual increase with increase in temperature and exhibits a change in slope at around 80°C. These observations constitute a clear evidence for viscoelastic liquid to weak gel transition in MILS sample at ~ 80°C.

#### 4.3.6 Reasoning for the Transition: Micellar structures Vs Association structures

The increase in turbidity and G' being greater than G''(Fig. 4.7) beyond 80°C are consistent with the formation of micellar network structures which are responsible for the weak gel behavior of MILS sample at  $T \ge 80^{\circ}$ C. Further, notice from Fig.4.7 that G' as well as G'' values measured during the heating cycle overlaps with those measured during the cooling cycle. This implies that the transition from viscoelastic liquid to weak gel state observed in the MILS sample is thermoreversible and the network structures formed in the sample are physical in nature [37]. Another important point to notice in Fig.4.7A is that G' values are much higher inviscoelastic fluid state as compared to that in weak gel state and also G' falls rapidly within the viscoelastic liquid state ( $<80^{\circ}$ C) as compared to the slow monotonous decay in the weak gel state ( $>80^{\circ}$ C). In order to know why the G'values are high in the viscoelastic liquid state, we have carried out rheological studies on BmimCl ionic liquid with 18.7 wt% LiCl salt (same concentration of salt as that in MILS sample and we refer this sample as ILS). The variation of G' with T is shown in Fig. 4.7B. Notice that at 40°C, ILS sample has a high value of G' which is known [18-20] to be due to large scale association structures present in the IL with LiCl which is shown schematically as an inset (top) in Fig.4. 7B. Further, G' falls steeply up to a temperature of  $80^{\circ}$ C and is due to the disintegration of large scale association structures into constituent units (see bottom inset in Fig.4. 7B).



Fig. 4.7A: G'&G'' of the MILS sample and B: G' of the ILS sample measured as a function of temperature with heating/cooling rate of 1°C/min, at  $\omega = 5$  rad/s and  $\gamma_0 = 0.2\%$ . Closed symbols represent cooling cycle and opened symbols for heating cycle. Insets in B: Top inset < 80°C shows schematically, the large scale associative structures in Ionic liquid with LiCl sample. Bottom inset >80°C the disintegration of associative structures into constituent units. Insets in A: Top inset < 80°C shows schematically the large scale associative structures of ionic liquid with LiCl sample. Bottom inset >80°C shows schematically the large scale associative structures of ionic liquid with LiCl salt and worm-like micelles in MILS sample. Bottom inset >80°C shows schematically the networks of worm-like micelles and the disintegration of associative structures of Ionic liquid with salt.

The high value of G'below 80°C in the MILS sample is mainly due to these large scale association structures of BmimCl with LiCl. Though the worm-like micelles are present, their contribution to G' is masked by the large scale association structures. Hence their presence cannot supported by low temperature (<80°C) rheological data presented in Fig. 4.1 A& C. However, the presence of worm-like

micelles in aqueous viscoelastic surfactant systems can be easily inferred from rheological data on viscoelastic aqueous surfactant systems [38] because the contribution to G' by water is not significant. In the high temperature phase, the contribution to G' in MILS sample is entirely due to the micellar network structures (see bottom inset of Fig. 4.7A) as the large scale association structures have disintegrated at these high temperatures. The G'' of ILS (not shown) is similar to that of MILS sample at 40°C and showed similar behaviors. Though G' is quite high in ILS and MILS samples at  $T < 80^{\circ}$ C, these samples flow yet very slowly under gravity due to their high viscosity [18-20].

We have subjected the MILS sample to small angle X-ray scattering (SAXS) and angle resolved static light scattering (SLS) investigations also with an aim to provide microstructural information in the viscoelastic liquid state and in the weak gel state. The strong absorption of X-rays by chloride ions present in the sample and high turbidity of the sample resulted in featureless scattering data in SAXS and SLS experiments. We believe that transmission electron microscopy (Cryo-TEM) and negative staining techniques might provide direct evidence for the microstructure but we could not employ these imaging techniques since they are not available to us. Such microstructural information is expected to provide crucial information in understanding the formation of micellar network structure.

#### 4.4 Conclusions

We have prepared viscous SDS-micellar ionic liquid solution with different concentrations of LiCl salt. Rheological studies on micellar ionic liquid with LiCl salt (< 13.1 wt%) showed the samples to be in a viscoelastic state in the entire range of temperature (40-120°C). 21.1 wt%, LiCl salt could not be dissolved completely in micellar ionic liquid. MILS sample with 18.7 wt% showed viscoelastic liquid for *T* 

 $<80^{\circ}$ C and a weak gel behavior at high temperatures ( $T > 80^{\circ}$ C). SANS measurements have revealed the presence of worm-like micelles in the viscoelastic state of the MILS sample. Turbidity and complex modulus measured as a function of temperature have revealed the transition from viscoelastic state to weak gel state occurs around 80°C. Rheological studies on BmimCl with 18.7 wt% concentrations of LiCl have indicated the presence of large scale association structures which are known to be responsible for the high viscosity of the sample at low temperatures (<80°C), disintegrate into constituent units at high temperature (>80°C). The weak gel state at high temperatures arises due to the disintegration of the associative structures at high temperature along with concomitant formation of micellar network structures. In many cases gelation occurs at lower temperatures whereas our observation of viscoelastic liquid turning into a weak gel upon increasing the temperature is yet another example for gelation occurring at high temperatures by sol-gel transition in complex ionic liquid systems [25] with additives. Though our studies indicate the micellar network formation in MILS sample at high temperatures, the exact mechanism for network formation is not known. We believe that present observations motivate studies for the elucidation of mechanism and direct evidences for the formation of micellar networks in ionic liquid systems with additives.

#### References

[1] N.A. Mazer, Laser light scattering in Micellar systems, in: R. Pecora (ed.), Dynamic Light Scattering: Applications of Photon Correlation Spectroscopy, Plenum Press, New York, 1985, pp. 305-346.

[2] R. Bandyopadhyay, A.K. Sood, Langmuir, 19 (2003) 3121-3127.

[3] M.S. Akhter, Colloids Surf. A, 150 (1999) 25-30.

[4] J.L. Anderson, V. Pine, E.C. Hag berg, V.V. Shears, D.W. Armstrong, Chem. Common, (2003) 2444-2445.

[5] A. Takada, K. Imaichi, T. Kagawa, Y. Takahashi, J. Phys. Chem. B, 112 (2008) 9660–9662.

[6] M.J. Monteno, F.F.C. Bazito, L.J.A. Siqueira, M.C.C. Ribeiro, R.M. Torresi, J. Phys. Chem. B 112 (2007) 2102-2109.

[7] B.G. Nicolau, A. Starlaugson, L. Fruchey, M.C.C. Ribeiro, M.D. Fayer, J. Phys. Chem. B, 114 (2010) 8350–8356.

[8] M. AnandhaRao, Rheology of Fluid and Semisolid Foods, Aspen Publishers. Inc, Gaithersburg, 1999.

[9] A.B. Rodd, C.R. Davis, D.E. Dunsten, B.A. Forrest, D.V. Boger, Food Hydrocolloids, 14 (2000) 445-454.

[10] Y. He, P.G. Boswell, P. Buhlmann, T.P. Lodge, J. Phys. Chem. B, 111 (2007) 4645–4652.

[11] Y. Kitazawa, T. Ueki, K. Niitsuma, S. Tmaizumi, T.P. Lodge, M. Watanabe, Soft Matter 8 (2012) 8067-8074.

[12] M.F. Helgeson, S.E. Moron, H.Z. An, P.S. Doyle, Nature Mater. 11 (2012) 344-352.

[13] W.Y. Shih, W.H. Shih, I.A. Aksay, J. Am. Ceram. Soc., 82 (1999) 616-624.

[14] E. Park, K. Song, Kor.-Aust. Rheol. J., 18 (2006) 67-81.

[15] M.B. Zayani, N.K. Ariguib, M.T. Ayadi, T.L. Grossiord, Colloids Surf. A, 316 (2008) 46-54.

[16] K. Ueno, K. Hata, T. Katakabe, M. Kondoh, M. Watanabe, J. Phys. Chem. B, 112 (2008) 9013-9019.

[17] K. Miyazaki, H.M. Wyss, D.A. Weitz, D.R. Reichman, Europhys. Lett., 75 (2006) 915-921.

[18] T. Shimada, N. Sakamoto, R. Motokawa, S. Koizumi, M. Tirrel, J. Phys. Chem. B, 116 (2012) 240-243.

[19] X.J. Cao, H.Z. Cummins, J.F. Morris, Soft Matter 6 (2010) 5425-5433.

[20] C.W. Macosko, Rheology: Principles, Measurements and Applications, VCH Publishers, New York, 1994.

[21] M. Grassi, R. Lapasin, S. Pricl, Carbohydr. Polym. 29 (1996) 169-181.

[22] R. Ndjouenkeu, J.O. Akingbala, R.K. Richardson, E.R. Morris, Food Hydrocolloids, 9 (1995) 165-172.

[23] D.R. Picout, S.B. Ross-Murphy, Thermoreversible and irreversible Physical gels from Biopolymers, in: Y. Osada, A.R. Khokhlev (eds.), Polymer gels and networks, Marcel Dekkar. Inc., New York, 2005, pp. 28-46.

[24] H. Rehage, H. Hoffmann, J. Phys. Chem. 92 (1988) 4712-4719.

#### **CHAPTER 5**

# Rheological studies on Silica-Ionic Liquid Nanocomposites as function of Concentration of Silica Nanoparticles and Temperature

### **5.1 Introduction**

In chapter 1, general introduction to colloidal dispersions with water and ionic liquids as solvents has been discussed. In chapter 4, rheological studies on micellar ionic liquid and its phase behaviour upon increasing the temperature and LiCl concentration has been presented. This chapter deals with rheological study on silica ionic liquid nanocomposite (SINC) as a function of concentration of silica nanoparticles and temperature. Colloidal dispersions of fumed silica is one of the most studied colloidal dispersion due to interesting properties of fumed silica [1]. Fumed silica is an amorphous form of silica and consists of fractal like aggregates of primary spherical non-porous silica nanoparticles of size 5-50 nm [2]. The aggregates consist of chainlike structures (Fig. 5.1 (a)) of silica nanoparticles and have high surface area in the range of 50 - 500  $m^2/g$ . The surface of the fumed silica consists of silanol groups (Si-OH) which decides the colloidal stability of fumed silica when dispersed in solvents. For example, if the fumed silica is dispersed in a polar solvent like ethylene glycol, results in a stable colloidal dispersion due to the hydrogen bonding between the surface silanol groups and solvent molecules. On the other hand when dispersed in a non polar solvent like mineral oil or silicone oil, silica aggregates form hydrogen bond among themselves to form flocs and further develop into three dimensional networks leading to gelation [3].

Fumed silica is widely used as a filler material in silicon-rubber based materials and is also a very important thickening agent and thixotropic agent for low molecular weight solvents. Gels of fumed silica in mineral oil and silicone oil are used as filling compounds in fibre optic cables [4]. However, the basic rheological studies on fumed silica dispersions in non-aqueous polar solvents are limited. Raghavan *et al* have studied the rheology of fumed silica dispersions formed in wide variety of polar organic solvents [5]. They reported the presence of solvation forces in stabilizing the dispersions. As discussed in chapter 1, ILs can be used as polar non aqueous solvents for dispersing fumed silica. Watanabe *et al* have studied the rheological behavior of



Fig. 5.1 (a) SEM photograph of fumed silica particles indicating their chain like structure (b) electron micrograph of fumed silica powder.Adopted from [6].

nanocomposite ion gels formed by dispersing different weight fractions of silica nanoparticles in EmimTFSI ionic liquid [7]. They observed that the nanocomposite to transform from a viscoelastic liquid to a gel state upon increasing the silica nanoparticles concentration. However, the effect of temperature on the rheological behaviour of nanocomposites has not been studied. Motivated by these studies, we have carried out detailed rheological studies as a function of temperature on silica-ionic liquid nanocomposites having different concentrations of silica nanoparticles and the results are presented in this chapter.

#### 5.2 Materials and methods

The ionic liquid, 1-Ethyl-3methylimidazolium bis(TriluromethylSulfonyl imide (Emim TFSI) (purity: 99.9%, density: 1.44 g/cm<sup>3</sup>, melting point: -15°C, viscosity, 30 cP (25 °C ) & water content < 0.1%) purchased from Ionic liquid Technologies, Germany was used as received. Fumed silica nanopowder was purchased from Sigma-Aldrich. The primary size of these nanoparticles is 14 nm and surface area, 300 m<sup>2</sup>/g. The silica nanopowder was dried under vacuum for 12 hours at 150°C prior to sample preparation. Required amount of silica particles are dispersed in the ionic liquid using high shear homogenizer (IKA- Ultra Turrax) at 24,000 revolutions/min for 30 minutes. After mixing, the samples were dried under vacuum for 12 hours at 100°C. MCR-301 Rheometer used for the study is discussed in chapter 2.

#### 5.3 Results and discussion

#### 5.3.1. Effect of silica nanoparticles concentration on the rheology of SINC samples

Fig 5.2(a), (b), (c) and (d) shows the physical states of the SINC samples with concentration of silica nanoparticles as 0.5 wt%, 1 wt%, 3 wt% and 5 wt% respectively. It is clear from Fig. 5.2 (a) & (b) that first two samples (0.5 wt% & 1 wt%) are flowing and the remaining two (3 wt% & 5 wt%) are non flowing. In order to characterize the rheological behaviour of these samples, frequency sweep measurements were carried out at  $25^{\circ}$ C in the linear viscoelastic region.

Fig. 5.3 shows the elastic modulus, G'and viscous modulus, G"as a function of frequency,  $\omega$  for 0.5 wt% and 1 wt% SINC samples at 25°C. It is evident that G'is slightly greater than G" in the measured  $\omega$  region (tan  $\delta = (G''/G') \sim 0.6$  to 0.1). Further, G' and G" show weak dependence on  $\omega$  and samples flow upon tilting (see Fig. 5.2 (a) & (b)). Fig. 5.3 (c) shows the yielding behaviour for samples with low yield stresses, 0.9 Pa and 3.7 Pa for 0.5 wt% and 1 wt% respectively. Upon increasing the stress amplitude, G'' exhibits a shallow peak whereas G' exhibits a monotonous decrease beyond the linear viscoelastic region. This type of yielding is observed in many weak gels and gel systems [8, 9]. This behaviour suggests that the breakage of big aggregates into dissipative smaller ones leading to the increase of G"upon increasing the stress amplitude [10].

These signatures are characteristics of a weak gel and are consistent with weak gel state reported for MILS sample in chapter 4. For both the samples, at high frequencies, G' is found to be frequency dependent while at low frequencies it exhibits frequency independence. Also, upon increasing the concentration from 0.5 wt% to 1 wt%, the frequency independent region of G' increases. This gives a clue that these samples have the tendency to form gel upon increasing the concentration of silica nanoparticles. However, a slight variation is observed in G'' when the concentration of



Fig. 5.2 Photographs of SINC samples having silica nanoparticles concentration (a) 0.5 wt%, (b) 1 wt%, (c) 3 wt% and (d) 5 wt%

silica nanoparticles is increased from 0.5 to 1 wt%.



Fig. 5.3G' (closed circles), G" (open circles) of SINC samples having silica nanoparticles concentration (a) 0.5 wt% and (b) 1 wt% as a function of frequency,  $\omega$  and (c) as a function of shear stress,  $\sigma$ 

Having characterized the flowing samples as weak gels, it is of interest to know the rheological state of non flowing samples. Towards this, we have carried out frequency sweep measurements on 3 wt% and 5 wt% samples (Fig. 5.2 (c) & (d)) in the linear viscoelastic region at 25°C and the values of G' and G'' as a function of  $\omega$  are shown in Fig. 5.4 (a) & (b) respectively. It is clear from the figure that G' is independent of  $\omega$  in the measured frequency region. Also, G' is much greater than G'' as compared to those samples which showed a weak gel behaviour. Further, the ratio of G'' to G'i.e. tan  $\delta \sim 0.05$  which is low as compared to 0.5 and 1 wt% samples. Further, G'' exhibits weak frequency dependence as compared to 0.5 wt% and 1 wt% samples and yielding behaviour which is shown in Fig. 5.4 (c).



Fig. 5.4G' (closed symbols), G" (open symbols) of SINC samples having silica nanoparticles concentration (a) 3 wt% and (b) 5 wt% as a function of frequency,  $\omega$  and (c) as a function of stress amplitude,  $\sigma$ 

Notice in Fig. 5.4 (c), G" shows a strong peak as compared to that of 0.5 wt% and 1 wt% samples. All these features are characteristics of gels [10, 11]. To summarize, SINC samples transform from a weak gel to gel state upon increasing the concentration of silica nanoparticles. Present results are consistent with Watanabe *et al* observations where they reported a transition from viscoelastic liquid state to gel state upon increasing the concentration of silica nanoparticles from 1 wt% to 3 wt% [7] except we observe a weak gel state at 0.5 wt% and 1 wt%. We attribute this difference to subtle differences in the sample preparation methods.



Fig. 5.5G' of SINC samples as a function of silica nanoparticle concentration. Lines are guide to eye.

Fig. 5.5 shows the variation of G' as a function of silica nanoparticles concentration. At low concentrations, the value of G' is smaller and increases almost linearly upto 1 wt%. Beyond this, G' starts increasing rapidly as weak gel transforms to gel state.

The reason for gelation upon increasing the silica particle concentration is understood as follows. Watanabe *et al* have showed that using Transmission Electron Microscopy (TEM) and Static Light Scattering experiment (SLS) [7] results silica particles in the ionic liquid Emim TFSI, undergo aggregation leading to clusters having fractal structure which percolate the entire volume of the IL as shown in Fig. 5.6. Using SLS measurements, they estimated a fractal dimension of 2.14 for the SINC samples which indicates that the formation of aggregates is governed by reaction limited cluster aggregation (RLCA) model.



Fig. 5.6In situ TEM image of SINC sample with 5 wt% silica nanoparticles. Adopted from [12]

Silica nanoparticles when dispersed in EmimTFSI ionic liquid undergo aggregation due to the poor colloidal stability [12]. However, at low concentrations (0.5 wt% and 1 wt%), the volume spanned by the clusters having less junction points, is less compared to the solvent volume and is responsible for the weak gel behaviour observed in 0.5 and 1wt% samples. When the concentration of silica particles increases, number of cluster increase with more junction points spanning the entire volume of the solvent leading to the gel behaviour for 3 wt% and 5 wt% samples and is shown schematically in Fig. 5.7.

#### 5.3.2. Effect of temperature on the rheology of SINC samples

Having characterized the SINC samples as a function of concentration of silica nanoparticles as weak gels at low concentrations and gels at high concentrations, it is of interest to study the effect of temperature on the rheological behaviour of these samples. Also, recent studies on the rheology of colloidal silica gels with temperature showed very interesting results [13, 14] which are given below.



Fig. 5.7 Illustration for the micro structural picture of gel networks in the ionic liquid by increasing the concentration of silica nanoparticles. For simplicity, the complex fractal networks are shown as curved lines.

Sanchez *et al* have reported the dynamic rheological studies on silica nanoparticles gels prepared in poly (ethylene glycol) dimethyl ether medium for different concentrations of fumed silica nanoparticles as well as a function of temperature [13]. They have observed an increase in *G'* for the fumed silica gels upon increasing the temperature from 25°C to 80°C. Wu *et al* have studied the dynamic rheology of fumed silica gels in the solvent, dodecane as a function of concentration of fumed silica particles and as a function of temperature [14]. Under small strains (< 10%) increase in *G'* with increase in temperature and for large strains (>10%), decrease of *G'* with increasing temperature was reported. These observations were attributed to the restructuring of fractal aggregates of silica particles under lower strains and

breakage of fractal networks under larger strains respectively. Hence we have carried out rheological measurements on SINC samples at three different temperatures.

Fig. 5.8 shows G' as a function of  $\omega$  at 25°C, 75°C and 125°C.for SINC sample having 1 wt% silica nanoparticles concentration. As discussed earlier, this sample at 25°C exhibited a weak gel behaviour. One expects these weak gels to melt upon increasing the temperature. However, G' increases to one order of magnitude upon increasing the temperature from 25°C to 75°C (Fig. 5.8). Further, G' exhibits frequency independence and the ratio of G" to G' is low (tan  $\delta \sim 0.05$  whereas 0.6 at 25°C). These are characteristics of a gel. With further increase of temperature from 75°C to 125°C, the same behaviour is observed as shown in the Fig. 5.8. 0.5 wt% sample also shows similar behaviour (not shown) upon increasing the temperature to 75°C and further to 125°C. These observations suggest that weak gels of SINC samples transforms to gels upon increasing the temperature, rather than melting.



Fig. 5.8*G* ' as a function of frequency,  $\omega$  of SINC samples having 1 wt% silica nanoparticles concentration at 25°C, 75°C and 125°C.

Fig. 5.9 shows G' as a function of  $\omega$  at 25°C, 75°C and 125°C for SINC sample having 5 wt% silica nanoparticles concentration. Like the previous sample, the 5 wt% sample continued to be in gel state as no melting has been observed. The G' value is found to increase with a concomitant decrease in the values of tan  $\delta$  (0.05 at 25°C, 0.03 at 75°C and 0.01 at 125°C) increased as seen from the Fig. 5.9. 3 wt% samples also showed similar behaviour with increase in temperature (which is not shown). It may be mentioned here that all the results reported here correspond to small value of oscillational strains (i.e. 0.05% to 0.2%).



Fig. 5.9*G* as a function of frequency,  $\omega$  of SINC samples having 5 wt% silica nanoparticles concentration at 25°C, 75°C and 125°C

The reason for the increase of G 'with respect to temperature may be explained in the following way. Since the SINC samples consist of network of fractal colloidal clusters of silica nanoparticles, the increase in temperature under small strain amplitudes make the networks more flexible, which favours the formation of more junction points as shown schematically in the Fig. 5.10. The increase in crosslinks makes the weak gel samples to become gels and the gel samples to become gels with increased strength upon increasing the temperature.



Fig. 5.10 Illustration for the micro structural picture of gel networks in the ionic liquid by increasing T. Red dots indicate junction points. For simplicity, the complex fractal networks are shown as curved lines.

# **5.4 Conclusions**

Silica ionic liquid nanocomposite (SINC) samples with different concentrations of silica nanoparticles have been prepared. The transformation from weak gel to gel has been observed for SINC samples as a function of concentration of silica nanoparticles. For the first time, a weak gel behaviour is observed for concentration of silica particles (<3wt%). The gel strength increased as a function of temperature for all SINC samples as a function of temperature. The temperature dependent behaviour of SINC samples is attributed to the increase of junction points of the fractal networks upon increasing the temperature.

#### References

- [1] H. E. Bergna, W. O. Roberts, Colloidal Silica Fundamentals and applications, CRCPress, Taylor & Francis group, New York (2006).
- [2] J. Norstorm, A. Matic, J. Sun, M. Forsyth, D. R. Macfarlane, Soft Matter, 6 (2010)2293.
- [3] T. Uchino, A. Aboshi, S. Kohara, Y. Ohishi, M. Sakashita, K. Aoki, Phys. Rev. B, 69 (2004) 155409.
- [4] S. R. Raghavan, S. A. Khan, J. Rheol, 39 (1995) 1311.
- [5] S. R. Raghavan, H. J. Walls, S. A. Khan, Langmuir, 16 (2000) 7920.
- [6] S. R. Raghavan, S. A. Khan, J. Colloid Interface Sci 185 (1997) 57.
- [7] K. Ueno, K. Hata, T. Katakabe, M. Kondoh, M. Watanabe, J. Phys. Chem. B, 112 (2008) 9013.
- [8] K. Miyazaki, H.M. Wyss, D.A. Weitz, D.R. Reichman, Europhys. Lett., 75 (2006)915.
- [9] T. Shimada, N. Sakamoto, R. Motokawa, S. Koizumi, M. Tirrel, J. Phys. Chem. B, 116 (2012) 240.
- [10] F. Yziquel, P. J. Carreau, P. A. Tanguy, RheolActa, 38 (1999) 14.
- [11] A.B. Rodd, C.R. Davis, D.E. Dunsten, B.A. Forrest, D.V. Boger, Food Hydrocolloids, 14 (2000) 445.
- [12] K. Ueno, S. Imaizumi, K. Hata, M. Watanabe, Langmuir, 25 (2009) 825.

[13] Sanchez AM, Colloidal gels of fumed silica: microstructure, surface interactions and temperature effects. PhD dissertation, University of North Carolina State, USA, 2006.

[14] X. J. Wu, Y. Wang, M. Wang, W. Yang, B. H. Xie, M. B. Yang, Colloid PolymSci, 290 (2012) 151.

#### **CHAPTER 6**

# SUMMARY AND CONCLUSIONS

This chapter summarizes the investigations carried out on the ionic liquid dispersions of an anionic surfactant, SDS with the addition of salt, LiCl and fumed silica nanoparticles as a function of temperature using rheology. There have been many studies on ionic liquids as solvents for organic synthesis, electrochemical methods etc. However, studies on ionic liquid dispersions with surfactants and nanoparticles are relatively limited. This thesis adds some important results in this direction. It can be seen from earlier chapters 3, 4 and 5, that how the results obtained from ionic liquid and its dispersions are different from conventional behavior reported in aqueous systems.

Chapter 3 reports the rheological behavior of the ionic liquid BmimCl as a function of temperature and surface activity of aqueous BmimCl solutions. The linear rheological behavior of BmimCl as a function of temperature yields a non-zero elastic modulus which is attributed to the presence of associative structures in BmimCl. Interestingly, the elastic modulus of BmimCl persisted even after its melting point (~68°C). This peculiar behavior of ionic liquids makes them special from conventional molecular solvents. Our work is the first study on BmimCl to explore the associative behavior of ionic liquids using rheology. Also, this ionic liquid, BmimCl has surface active property as its cation has butyl alkyl chain. Surface tension studies on aqueous BmimCl solutions as a function of BmimCl concentration revealed that BmimCl is surface active and reduces the surface tension of water.

Chapter 4 presents the rheological studies on the MILS samples having different concentrations of LiCl salt. BmimCl dispersions of sodium dodecyl sulfate (>CMC) with different concentrations of LiCl (4.8, 9, 13.1 & 18.7 wt%) salt were prepared and

rheological studies have been carried out at different temperatures. Through the linear and nonlinear rheological studies, for the first time, MIL sample with 18.7 wt% LiCl exhibited a transition from viscoelastic liquid state to weak gel state upon increasing the temperature. However, samples with lower concentrations of LiCl (4.8, 9 &13.1 wt%) showed no transition and remained in viscoelastic liquid state. Temperature sweep dynamic rheological measurements on MILS sample at cooling and heating cycle revealed that this transition is thermoreversible. Turbidity and complex modulus as a function of temperature showed the transition temperature to be around 80°C as these two parameters undergone a slope change at that temperature. Small Angle Neutron Scattering experiments revealed the presence of wormlike micelles.

Chapter 5 presents the rheological studies on the SINC samples as a function of temperature and concentration (0.5 - 5wt%) of silica nanoparticles. SINC samples with lower concentrations of silica nanoparticles (< 3 wt%) exhibit a weak gel behavior whereas samples with higher concentrations (> 3 wt%) exhibit a strong gel behavior. This transformation is attributed to the formation of more fractal colloidal networks upon increasing the concentration. SINC samples with lower concentrations of silica nanoparticles (< 3 wt%) transform from a weak gel behavior to strong gel behavior upon increasing the temperature. For, samples with higher concentrations of silica nanoparticles (> 3 wt%), gel strength is increased upon increasing the temperature. This behavior of these samples is attributed to the formation more junction points in fractal colloidal networks upon increasing the temperature.

The important findings of this thesis are given below.

• The ionic liquid BmimCl is synthesized and its rheological properties have been studied as a function of temperature. Flow measurements have revealed that it is a Newtonian fluid. The presence of non zero elastic modulus obtained beyond

the melting point (68°C) by dynamic rheological measurements revealed the presence of dynamic network structures over a wide range of temperature.

- Surface tension measurements on aqueous BmimCl revealed that BmimCl does not form micelles in water.
- Highly viscous SDS-micellar ionic liquid (4.45 wt%) dispersions with different concentrations of LiCl salt 4.8, 9, 13.1&18.7 wt% have been prepared. Our rheological studies have revealed, for the first time, that the sample with 18.7 wt% LiCl concentration exhibits a weak gel state at high temperatures which transforms to a viscoelastic liquid state upon lowering the temperature.
- Small angle neutron scattering (SANS) measured on the MILS sample carried out at different temperatures have revealed the presence of worm like micelles.
- Rheological studies on BmimCl with 18.7 wt% concentrations of LiCl have indicated the presence of large scale association structures which are known to be responsible for the high viscosity of the sample at low temperatures (<80°C), disintegrate into constituent units at high temperature (>80°C). The weak gel state observed at high temperatures arises due to the disintegration of the association structures at high temperature along with concomitant formation of micellar network structures.
- Silica-ionic liquid nanocomposite has been prepared by dispersing different amounts of silica nanoparticles in Emim TFSI ionic liquid. Dynamic rheological studies on SINC samples with different concentrations of silica nanoparticles have been carried out at different temperatures and the elastic modulus of the samples is found to increase upon increasing the temperature.
- SINC samples with lower concentrations of silica nanoparticles (<3 wt%) exhibit a weak gel behavior whereas samples with higher concentrations (>3

wt%) exhibit a strong gel behavior. This transformation is attributed to the formation of fractal colloidal networks upon increasing the concentration.

Unlike aqueous micellar systems, our micellar system (MILS) is different in the phase and rheological behavior. Usually, the colloidal dispersions exhibit a liquid like behavior at elevated temperatures and gel behavior upon cooling.
MILS showed weak gel behavior and SINC samples showed strong gel behavior at high temperatures.

#### Scope for future study

The study on MILS sample was carried out only with the variation of concentration of LiCl salt. However, we did not carry out as a function SDS concentration. Also, due to experimental limitations, we are unable to perform SANS measurements on MILS sample above 80°C. Rheological measurements on SINC sample were carried out without any additive. Studies showed that cationic surfactant CTAB and non ionic surfactants dissolved in IL, Emim TFSI. It will be interesting to investigate the effect of these surfactants on aggregation of silica nanoparticles in Emim TFSI and also the effect of temperature. Future experiments on MILS samples and SINC samples will be planned in these directions.

# LIST OF PUBLICATIONS

# **Publications in Journals**

1)"Thermo-reversible Viscoelastic to Weak Gel transition in a micellar-ionic liquid with salt", **K. Saravanakumar**, B. V. R. Tata and V.K. Aswal, Colloids and Sufaces A, **414** (2012) 359-65.

2) "Abnormal Thermo-rheological behaviour observed for Silica Ionic Liquid Nanocomposites", **K. Saravanakumar** and B. V. R. Tata (Manuscript under preparation)

3) "Rheological behaviour of ionic liquid BmimCl as a function oftemperature", **K. Saravanakumar** and B. V. R. Tata (Manuscript under preparation).

# Publications in Conference proceedings

1) "Thermo-reversible Viscoelastic to Weak Gel transition in a micellar-ionic liquid solution", **K. Saravanakumar**, B. V. R. Tata and K. A. Venkatesan, DAE-Solid State Physics Symposium, Editors, A.K. Rajaraman, A.B. Garg and G. P. Kothiyal, Vol.54, p. 257-8, 2009, Vadodara, India.

2) "Effect of Temperature on Soft Glassy Behaviour of Silica-Ionic Liquid Nanocomposite" **K. Saravanakumar** and B. V. R. Tata, IEEE Xplore Conference Publications, ICONSET (2011) 40-43.

# **Presentations in Conferences**

1) "Rheological characterization of Sol and Gel states in amicellar-ionic liquid solution", **K. Saravanakumar**, B. V. R. Tata, J. Brijitta and K. A. Venkatesan, International Conference on Sol-Gel processes for Advanced Ceramics (SGPAC), October 11-14, 2009, Kalpakkam, India.

2) "Thermo-reversible Viscoelastic to Weak Gel transition in a micellar-ionic liquid solution", **K. Saravanakumar**, B. V. R. Tata and K. A. Venkatesan, DAE-Solid State Physics Symposium (SSPS), December 14-18, 2009, Vadodara, India.

3) "Rheological studies on micellar-ionic liquid as a function of temperature", **K. Saravanakumar**, B. V. R. Tata and K. A. Venkatesan, SERC School-cum-Symposium on Rheology of Complex Fluids, January 04-09, Chennai, India.

4) "Effect of Temperature on Soft Glassy Behaviour of Silica-Ionic Liquid Nanocomposites", **K. Saravanakumar**, B. V. R. Tata and K. A. Venkatesan, International Conference on Nanoscience, Engineering and Technology, November 28-30, 2011, Chennai, India.