

**RHEOLOGY AND MICROSTRUCTURE OF STABLE CONCENTRATED
IONIC LIQUID COLLOIDAL SUSPENSIONS**

by

Jingsi Gao

A dissertation submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemical Engineering

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IONIC LIQUID COLLOIDAL SUSPENSIONS**

by

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ABSTRACT

Astronauts are constantly threatened by impact from micrometeorite and orbital debris (MMOD) when conducting extra-vehicular activities (EVA) in low Earth orbit (LEO). These threats have already become a major challenge to long-term missions and deep space exploration. Shear thickening fluids (STFs) demonstrate an abrupt increase in viscosity with applied high shear stress, improving their ability to dissipate energy and making them good candidates for protective body armor. In my thesis work, a novel STF formulation in ionic liquid has been developed to improve the resistance of EVA suit against threats from ballistic, puncture, and hypervelocity MMOD impacts. Ionic liquids serve as the solvent phase for the STF formulations because of their low volatility and stability over a broad range of temperatures. However, dispersing colloidal particles in ionic liquids can be challenging because the high ionic strength of ionic liquids screens the electrostatic stabilizing forces that are typically important for stabilizing colloidal dispersions in polar solvents.

Stable nanoparticle dispersions in the ionic liquid $[\text{C}_4\text{mim}][\text{BF}_4]$ are created through surface coatings (*e.g.*, fluorinated alkyl chains, alcohol), which induce solvation layering around the particles. Solvation layers are initiated by hydrogen bonds between the anion groups $[\text{BF}_4]^-$ and the functionalized particle surface, providing a stabilizing steric repulsive inter-particle force. Rheology, electron microscopy, dynamic light scattering (DLS), and small-angle neutron scattering (SANS) are employed to determine the thickness of the solvation layers and the

microstructure of dispersions for different coating systems. A quantitative model based on analysis of SANS data is developed to evaluate the inter-particle interactions and the thickness of the solvation layers. Additionally, the rheological behavior of dispersions is controlled by tuning the strength of surface hydrogen bonding with different surface chemistry. The influence of temperature on the thickness of solvation layers and particle interactions is also investigated through rheology, DLS, and SANS studies. Destabilization phenomena (from stable dispersion to unstable gel) are identified due to the change of interfacial structure with increasing temperature. Furthermore, the influence of impurities (*i.e.*, water) on the microstructure and thermodynamic properties of ionic liquid are studies using SANS and small-angle x-ray scattering (SAXS) techniques. A phase diagram for ionic liquid aqueous solutions (microphase separation, phase inversion, and micelle formation) is constructed, revealing similarities to traditional oil-water-surfactant systems. This understanding of ionic liquid phase behavior and formation of solvation layers is critical for the formulation of colloidal dispersions in ionic liquids with a specific rheological profile. Ionic liquids based STF-Kevlar[®] nanocomposites are shown to provide superior puncture resistance in lab scale quasi-static puncture tests. The fabricated nanocomposites are proven to provide better protection than traditional Kevlar[®] without compromising the flexibility. The results of the present research demonstrate the feasibility of STF-Kevlar[®] nanocomposites for astronaut protection and identify technological challenges that still need to be addressed.

Chapter 1

INTRODUCTION

1.1 Motivation

Millions of micrometeoroids and orbital debris (MMOD) particles are traveling at hypervelocity speeds averaging 10 km/s in low-earth orbit.¹ MMOD particles in the near-Earth space environment are comprised of naturally occurring micrometeoroids originated from comets and asteroids, and man-made debris of fragmented rocket bodies and spacecraft parts created during the space exploration in the past 60 years. MMOD particles continually collide with spacecraft and satellites. Although spacecraft and satellites can avoid collisions with large and trackable MMOD particles (usually larger than 10 cm) by maneuvering around,² smaller MMOD particles (1 cm to 10 cm in diameter) are not easy to track; collision with these particles can cause severe damage. Furthermore, extra-vehicular activity (EVA) exposes astronauts to potential MMOD impacts ranging from secondary lunar ejecta at a speed of 0.1-1 km/s to orbital debris at a speed of 1-15 km/s to micrometeoroids at a speed of up to 70 km/s,¹ which becomes a life threatening risk to astronauts performing EVA in space. What's worse, the MMOD threat is still growing. With more satellites being launched, explosion of non-functional satellites, and high-speed collision between existing orbital debris, more and more debris is created. The threat of MMOD impact on active spacecraft and EVA suits has already become a major challenge to long-term missions and deep space exploration.

In addition to MMOD impact, space suits also are exposed to damages arising from other physical hazards such as tools, sharp edges on handrails or surface elements.³ It may be possible to add bulky or stiff individual layers to protect against each of the different types of threat for specific cases,⁴ this approach will detrimentally increase the weight and reduce the flexibility of the EVA suit, which is definitely undesirable. Thus, flexible, lightweight, and multi-threat protective materials are imperative to provide enhanced protection against multi-threats without compromising the weight or flexibility of the space suit.

Shear thickening fluid (STF)-nanocomposites (typically referred as STF-ArmorTM) are a promising candidate for use in advanced EVA suits to address these challenges because of their flexibility, lightweight and ability to protect against multiple mechanical threats. STF-ArmorTM is a protective nanocomposite where STF is intercalated into the protective textile. This material has been demonstrated to provide enhanced protection against simulated hypervelocity MMOD impacts, with higher energy absorption capability than prototype lay-ups of the standard thermal micrometeoroid garment (TMG).⁵ However, the current generation of STF-ArmorTM uses STF formulation of dispersed colloidal particles in polyethylene glycol as the carrier medium, which solidifies at low temperature and evaporates under vacuum. Therefore, it is crucial to develop new STF formulations to withstand vacuum and extreme low temperature space environment. Ionic liquids are emerging candidates for the solvent phase of STF formulations for space applications because of their thermal stability and low volatility.⁶ However, achieving stable ionic liquid-based STFs can be challenging because the high ionic strength of the ionic liquids screens the electrostatic stabilizing forces that are typically important for dispersing particles

in polar solvents. Hence, understanding the particle interactions and engineering the particle phase chemistry to achieve stable and desirable shear thickening fluids in ionic liquids are important.

1.2 Shear Thickening Colloidal Suspensions

Shear thickening is one of the most significant changes evident in stable colloidal dispersions, which is marked by an increasing viscosity with increasing shear stress or shear rate.⁷⁻⁹ As opposite to shear-induced aggregation, shear thickening herein is reversible and relevant to numerous industrial products and processes, such as paints, pharmaceuticals, lubricants, microabrasives, paper coating, and spraying which are often processed at high shear rate and shear stress. Shear thickening phenomena oftentimes need to be avoided as they can cause equipment damage and failure, as well as irreversible aggregation of dispersion particles. However, they are found in applications for damping and control devices,¹⁰⁻¹² electrorheological fluids,¹³ stab and puncture resistance flexible composites,¹⁴⁻¹⁵ and enhanced soft body armor.¹⁵

Three distinguished rheological behaviors: Newtonian, shear thinning, and shear thickening, exist for the concentrated near hard-sphere colloidal dispersions during shear flow, and their corresponding microstructures are shown in Figure 1.1. The non-Newtonian flow behavior is the direct consequence of the microstructural rearrangement of the near hard-sphere particles during shear flow. At low shear rate, the suspension is at equilibrium. Colloidal particles are driven by Brownian motion governed by the thermodynamic forces. The random collisions between particles give rise to the natural resistance to flow. Thus, an elastic stress from Brownian motion provides the driving force to move the microstructure back to equilibrium.¹⁶⁻¹⁸ The Brownian stress is linear with the shear rate, which results in a Newtonian, zero shear

viscosity in the linear regime. When the shear rate increases to moderate values, the microstructure exhibits anisotropic behavior as particles spatially rearrange to reduce their interaction so as to flow with less resistance. The dispersion exhibits shear thinning, as the stress contributions from the thermodynamic forces no longer increase linearly with increasing shear rate. At even higher shear rates, the suspension shear thickens as the viscosity increases reversibly, due to an increasing contribution from the hydrodynamic interactions between the particles in suspensions.

These non-Newtonian flow behaviors can be understood through the analogy to traffic with cars acting as particles.⁹ The equilibrium state is analogous to driving cars in a parking lot. The traffic flow is limited as individual cars are watching out for other cars from any direction. With increasing shear rates, particles behave like cars merging on the highway. The particles flow streamlined as cars follow each other and the increasing efficient transport of colloidal particles reduces the viscosity of dispersions. However, when the shear rate reaches the non-linear regime, the microstructure of particles is similar to traffic collisions or traffic jam, in which the well organized and low resistance flow is disrupted. The difficulty of cars (particles) flowing around each other increases the resistance to flow and the viscosity increases.

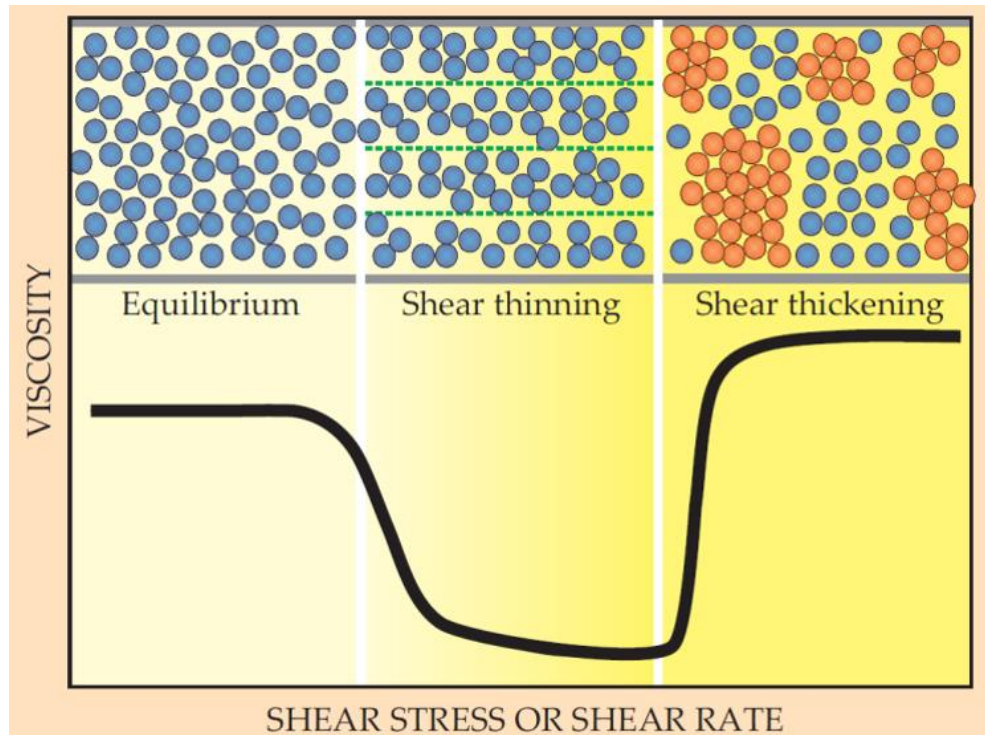


Figure 1.1: Illustration the microstructure of shear thickening fluids explaining the transition to shear thinning and shear thickening during shear flow. The change of microstructure corresponds to three distinguish regions: (1) equilibrium: the particles collide randomly due to thermodynamic forces; this Brownian motion of particles makes them naturally resistant to flow. (2) shear thinning: particle become organized along the shear flow direction at moderate shear rate or shear stress, which lowers their viscosity. (3) shear thickening: hydrodynamic interactions between particles dominate over thermodynamic forces, resulting in transient fluctuation of particles associating as “hydroclusters”. An abrupt increase in viscosity is resulted from the difficulty of particles flowing around each other in the flow field. Adapted with permission from Wagner, N. J.; Brady, J. F. *Physics Today* 2009, 62 (10), 27-32. Copyright 2009 American Physical Society.

The mechanism of reversible shear thickening in stable colloidal dispersions have been studied through numerous pioneering simulations^{16, 19-22} and experiments combining rheology with scattering techniques, such as rheo-optics,¹⁸ and small-angle

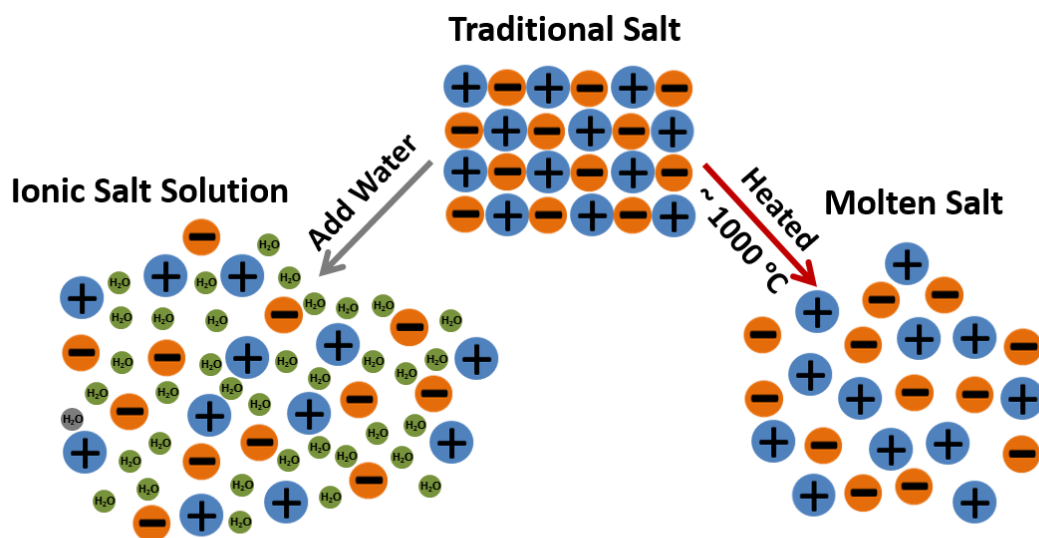
neutron scattering (SANS).²³⁻²⁷ The competition between the conservative thermodynamic force and the viscous hydrodynamic force acting between the particles in suspension during shear flow is critically important to understand and predict the non-equilibrium shear rheology. The shear thickening response is the result of an increasing contribution from the hydrodynamic interactions between the particles in suspensions. At high shear rate/stress, colloidal suspensions are dominated by short-range lubrication interactions which lead to density fluctuations of particle and ultimately, stress-bearing clusters named as “hydroclusters”.^{16, 24, 28} The transient density fluctuations are first predicted by Stokesian dynamic simulations,^{16, 19-22} and then observed experimentally by rheo-optical,¹⁸ neutron scattering techniques,²³⁻²⁷ and stress jump measurements.²⁹⁻³⁰ Note that these clusters caused by lubrication hydrodynamics are not permanent aggregates; they are transient density fluctuations, which form and break during shear.

The shear thickening rheological properties of the concentrated colloidal dispersions have been investigated by both experimental and theoretical works.^{16, 18-27} The relationship between particle properties and shear thickening has provided insight into the prediction of dispersion properties. Barnes summarized many parameters that would influence shear thickening, including particle size, particle concentration, polydispersity, shape, particle interaction, and the properties of the solvent.⁷ The shear thickening behavior strongly depends on the particle size, with the critical stress for shear thickening scaled as the inverse of the particle radius squared.²⁸ The non-Newtonian flow behavior can be observed at volume fraction above 0.2 for monodispersed spherical colloidal dispersions, while discontinuous shear thickening starts from 0.5 volume fraction. It is found that the required particle concentrations

for these transitions increase for polydisperse systems,³¹ while anisotropy in particle shape decreases the required concentration or increases the strength of shear thickening at a given concentration.³²⁻³³ As the separation between hydroclustered particles is of the order of a few nanometers, shear thickening behavior directly reflects the short-range particle interaction.^{22, 34} It has been found that when the range of the repulsive force between particles approaches 10% of the particle radius, shear thickening is effectively eliminated. Thus the shear thickening can be controlled by tailoring particle properties and particle interactions.

1.3 Ionic Liquids

Room temperature ionic liquids (ILs) are defined as salts that are liquids at or near room temperature. Similar to traditional salts, such as sodium chloride (NaCl), ionic liquids are composed only of ions: organic cations and inorganic or organic anions.^{6, 35} ILs are pure molten salts at room temperature without the presence of any molecular solvents; this makes them fundamentally different from ionic salt solutions, which are the aqueous solutions of salts dissolved in water. In traditional salts, small and symmetrical cations and anions are packed together tightly, resulting in extremely high melting temperature (800 to 1000 °C). In contrast, the organic cations and anions of ILs are typically big and unsymmetrical, which cannot get close enough to crystallize, as shown in Figure 1.2. This inability to form a solid is known as frustrated crystallization, and as a result, many ionic liquids are fluids at room temperature.³⁶



**Room Temperature Ionic Liquids:
Molten Salt at or near to Room Temperature**

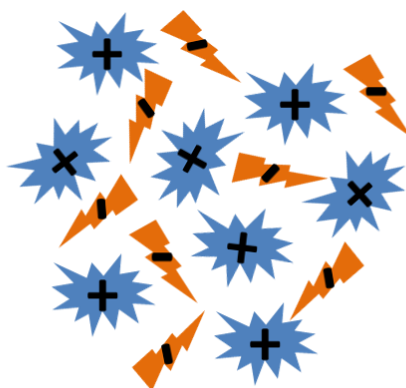


Figure 1.2: Schematic illustration of structural difference between traditional salts and ionic liquids. Traditional salts are crystal solid with small and symmetrical ions at room temperature. They can form ionic salt solution when dissolved in water or be melted to liquid form when heated up to around 1000 °C. Room temperature ionic liquids are molten salts at or near room temperature. They are composed of only ions, which are typically large and unsymmetrical, resulting in non-crystallized structure.

Ionic liquids exhibit unique physicochemical properties, such as negligible vapor pressure, non-flammability, high thermal and chemical stability, a broad electrochemical window, a wide range of liquid state, and good electrical conductivity.^{6, 37} The most fundamental characteristic of ionic liquids is their low volatility. Molecular solvents, such as water and alcohol, are composed of neutral molecules with van der Waals attraction force. When the molecules at the surface obtain enough energy to overcome the van der Waals attraction through heating, the molecules enter the gas phase and evaporate into the atmosphere. Unlike the molecular solvents, the interactions between ions in ionic liquids are through ionic bonds, which are several orders of magnitude stronger than the van der Waals force. It is unlikely for the ions to overcome such stronger attraction to evaporate into the atmosphere under normal condition when heated.³⁶ Thus, the vapor pressure of ionic liquids is negligible in comparison to molecular solvents. This low vapor pressure induces the non-flammability of ionic liquids; thus it is much safer to use ionic liquids in industrial processes when large quantities of solvents are needed.

In addition to the low volatility and non-flammability compared with traditional volatile organic compounds (VOCs), another important advantage of ionic liquids is their great capability of dissolving numerous substances due to their high and tunable polarity. Cellulose, polymers and metal salts, which are otherwise only soluble in a few solvents, can be dissolved in ionic liquids. Ionic liquids are the only solvents that are able to dissolve coal.³⁶ Their capability to dissolve substances that are traditionally considered insoluble enables the access to new chemistry and novel chemical reactions, which were impossible before due to the insolubility of reactants into the same liquid phase. More importantly, ionic liquids do not dissolve glass or

stainless steel.³⁶ Thus, they are stored in glass bottles and stainless steel rheometer tools are used when measuring their rheological properties in this dissertation.

Another key advantage of ionic liquids is that their properties can be tailored as desired. Ionic liquids offer great flexibility in the design of both the cationic and anionic structures and their combinations, thus they have been termed as “designer solvents”.³⁶ Through manipulation of their cations, anions, or both, ionic liquids can be designed to possess specific properties. In contrast, the application range of conventional molecular solvents is limited because their properties cannot be easily tuned. Additionally, there are only about 600 conventional molecular solvents in use, while there are at least a million possible simple ionic liquids through the different combination of various cations and anions.³⁵⁻³⁶ The most commonly used cations and anions are shown in Figure 1.3. The wide variety of available cations and anions provide a high flexibility in material design. Furthermore, at least a billion binary ionic liquids and 10^{18} ternary ionic liquids are possible when considering the mixtures of ionic liquids.³⁶

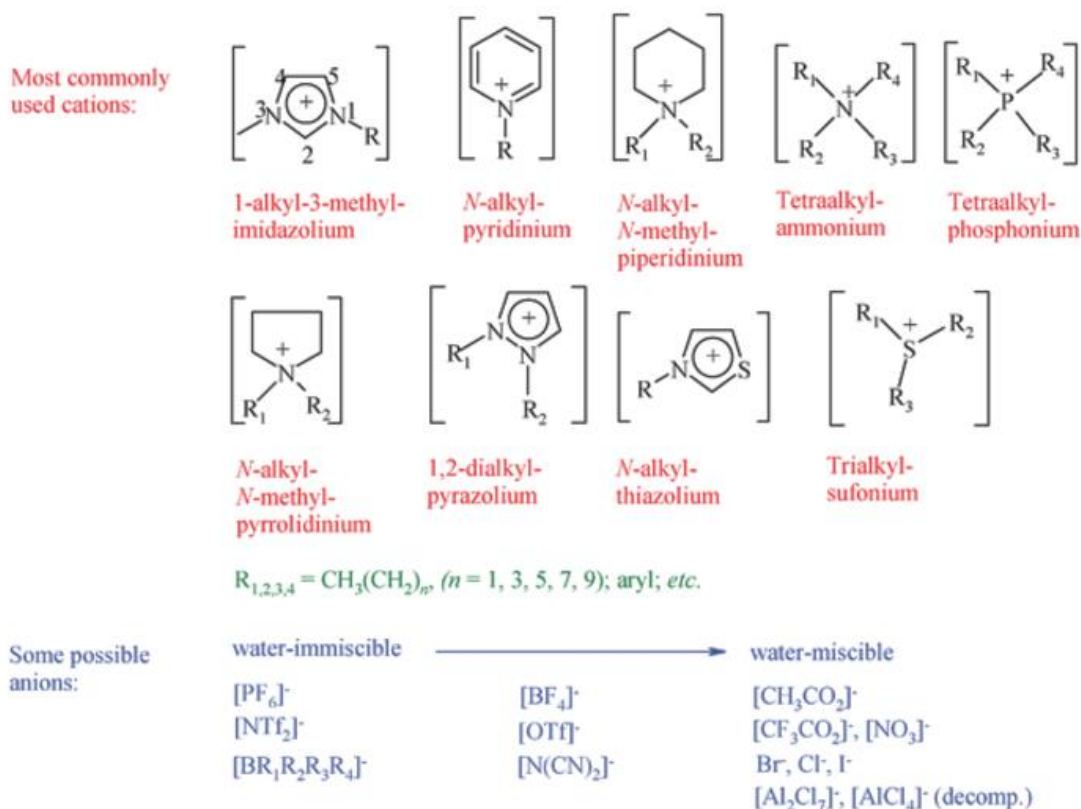


Figure 1.3: List of commonly used cations and anions in ionic liquid systems.³⁸ The abbreviation $[\text{C}_n\text{mpyr}]^+$ represents the 1-alkyl-1-methylpyrrolidinium cation, where the index n represents the number of carbon atoms in the linear alkyl chain. $[\text{P}_{wxyz}]^+$, $[\text{N}_{wxyz}]^+$, and $[\text{S}_{xyz}]^+$ represent tetraalkylphosphonium, tetraalkylammonium and trialkylsulfonium cations, respectively, where the indices w , x , y and z indicate the length of the corresponding linear alkyl chains. Adapted with permission from Plechkova, N. V.; Seddon, K. R. Chem. Soc. Rev. 2008, 37 (1), 123-150. Copyright 2008 The Royal Society of Chemistry.

This incredible diversity enables the solvent to be designed and tuned to obtain optimal substrate solubility, selectivity, yield, product separation, and even enantioselectivity.^{6, 39} Ionic liquids can serve as media for a wide range of organic and inorganic reactions,⁶ can dissolve enzymes,⁴⁰ can form versatile biphasic systems for

separations.⁴¹ Ionic liquids can be highly conductive, and form both polymers and gels for device applications.⁴²⁻⁴³ Ionic liquids have received considerable interest in various fields including separations,⁶ catalysis,^{6, 37, 44-45} electrolytes,^{43, 46} heat transfer,⁴⁷⁻⁴⁸ and drug delivery.⁴⁹ Their unique physicochemical properties suggest they can be used as an environmentally friendly “green” alternative for conventional organic solvents,^{6, 37, 44} as lubricants for space and high vacuum environments,⁵⁰⁻⁵² as separation media for batteries, fuel cells,⁴⁵ dye sensitized solar cells,⁴³ and more recently, for carbon capture from flue gases in industrial scale.⁵³

In many of these applications, the ionic liquids are exposed to water and non-ideal thermodynamic properties in mixture properties are evident.⁵⁴ Thus, the physicochemical properties of ionic liquids and their mixture with organic/inorganic solvents are interesting both from practical and theoretical point of view and are of importance for their applications.^{38, 55-56} Non-ideal thermodynamic properties in mixture properties such as density and viscosity have been reported for the ionic liquids [C_nmim][BF₄] with various molecular solvents,^{9, 54, 57-65} such as water, and alcohols, through systematic studies. Rodriguez *et al.* studied the temperature and composition dependence of the density and viscosity of aqueous solutions of a series of 1-ethyl-3-methylimidazolium with varying anions. A trend between excess volume and viscosity is suggested, which can be used for prediction of physical property.⁶⁶

Water is a common contaminant in ionic liquids,⁶⁷ especially for hydrophilic ionic liquids, which have the tendency to mix with, or dissolve in water, such as [C₄mim][BF₄]. The thermodynamic properties of ionic liquids can be significantly altered by addition of trace amount of water.⁶⁸⁻⁶⁹ Therefore, knowledge of excess

thermodynamic properties of ionic liquids aqueous solutions provides insight into the molecular interactions in these mixtures and aids in developing structure-property relationships. With these knowledge, the properties of ionic liquids can be optimized for specific applications.^{38, 70-71}

For example, the density and viscosity of binary mixtures of [C₄mim][BF₄] with water have been investigated and found to be non-ideal over the entire composition range.^{54, 57-58} These mixture non-idealities are attributed to the hydrogen bonds between water molecules and the [BF₄]⁻ anions, which affects the microstructure of the ionic liquid.⁶⁸ The molecular structure and interactions in mixtures of ionic liquids and water have been studied by experimental techniques,⁷²⁻⁷⁵ and complemented by molecular simulations.⁷⁶⁻⁷⁷

Because of the amphiphilic structure of ionic liquids, similar to surfactant, they can self-assemble into micelle-like structures when diluted in solvents. The aggregation of ionic liquids is evident and characterized using various techniques, including SANS,^{75, 78} NMR,^{63, 69} surface tension and conductivity measurements.⁷⁵ The conformational changes in a variety of ionic liquids induced by the self-aggregation of ionic liquid are shown to depend on the aromatic ring, alkyl chain, counter ions, and their interactions with water.⁷³

In addition, the opposite end of the composition spectrum, rich in ionic liquids, is equally interesting, however less well understood.^{76, 79-80} The interaction between the anion and water is found to generally dominate for salt-rich region of [C₄mim][BF₄]-water mixtures. Individual water molecules form hydrogen bonds with two [BF₄]⁻ anions without substantially disrupting the nanoscale structuring of the ionic liquid.^{72, 75, 80-81} However, water dimers and even larger clusters start to form

with increasing water content. Furthermore, the strong electrostatic interactions between the cations and anions is gradually disrupted with increasing water addition, resulting in the disturbed nanostructure of the ionic liquid.⁷⁶ Further addition of water leads to a micro-phase transition from ionic liquid polar networks to water clusters in the ionic liquid, then to ionic liquid self-aggregates in water, and finally to dilute ionic liquid electrolytes in water. These phase transitions and properties are revealed by molecular simulation⁷⁶ and experiments,^{75, 79-81} including FTIR,⁷⁹ Raman and IR spectroscopy⁸⁰ *et al.* It is confirmed that water aggregation in ionic liquids is mainly determined by association of the water with ionic groups in the ionic liquids and less by the hydrophobicity of the cations.

1.4 Ionic Liquids Colloidal Suspensions

Colloidal suspensions in ionic liquids have attracted increasing attention in recent decades as many applications of ionic liquids require successfully dispersing nanoparticles across a broad range of conditions. There are numerous research studies of colloidal systems in ionic liquids including nanoparticle synthesis,⁸²⁻⁸³ phase transfer,⁸⁴ catalytic reactions medium as a “green” solvent,^{6, 37, 44, 85} and the self-assembly of surfactants.⁸⁶⁻⁸⁹ The stability of nanoparticle and the associated suspension microstructure is critical in determining the suspension rheology and controlling aggregation, gel and glass formation. However, particle stabilization in ILs is challenging because their ionic nature screens electrostatic repulsive forces.

Particle dispersion and stability in ILs depends on the specific chemical composition of the ionic liquids as well as the surface chemistry of the particles.⁹⁰⁻⁹⁴ Hydrophilic fumed silica particles are reported to be well dispersed in [C₄mim][BF₄] displaying shear thickening.⁹¹ However, unstable dispersion with strong shear

thinning and yielding behavior is discovered for the same hydrophilic fumed silica particles in 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[\text{C}_2\text{mim}][\text{NTf}_2]$).⁹¹ In addition, aggregation and gelation are reported for hydrophobic fumed silica particles in $[\text{C}_4\text{mim}][\text{BF}_4]$.⁹¹ These dispersion phenomena demonstrate that it is non-trivial to disperse particles into ionic liquids.

The interaction between particles in dispersions is typically evaluated by Derjaguin-Landau-Verwey-Overbeek (DLVO) theory, which accounts for van der Waals attraction and electrostatic repulsion between particles in solution.⁹⁵ Due to the high ionic strength in ionic liquids, the electrostatic repulsion between silica particles is effectively screened. Thus, the electrostatic stabilization is not sufficient to stabilize particles in ionic liquids against the van der Waals attraction between particles.⁹⁶ Figure 1.4 gives an example of screened electrostatic repulsion between two silica particles of ~ 100 nm size in ionic liquid $[\text{C}_4\text{mim}][\text{BF}_4]$. Compared with silica particles in salt aqueous solution of low salt concentration, silica particles in $[\text{C}_4\text{mim}][\text{BF}_4]$ have similar van der Waals attraction, but significantly screened electrostatic repulsion. The screening of the electrical potential and electrical double layers at charged solid surfaces in ionic liquids and molten salts⁹⁷ has been investigated using experiments⁹⁸ and simulations.⁹⁹⁻¹⁰⁰

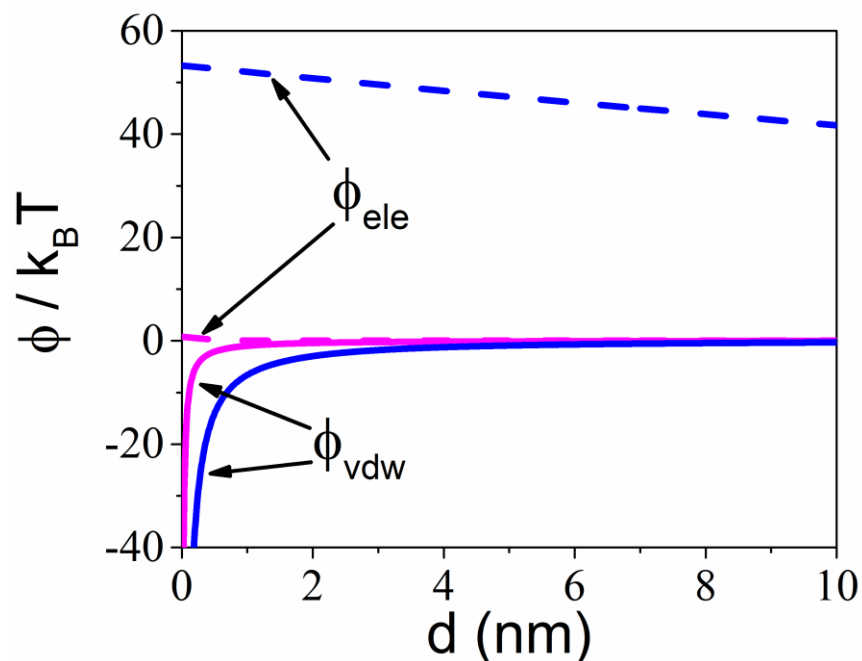


Figure 1.4: Calculated van der Waals attractive (solid line) and electrostatic repulsive (dash line) potential profiles between two silica particles at $T = 25\text{ }^{\circ}\text{C}$ for silica particles in $[C_4mim][BF_4]$ (magenta) and in 0.1 mM NaCl aqueous solution (blue).

Despite the screening of the electrical repulsion, hydrophilic fumed silica particles are reported to be dispersed into an aprotic ionic liquid, $[C_4mim][BF_4]$ in the absence of any stabilizer.^{91, 101-102} Altin points to the unique properties of ILs with respect to their nanoscale structure, such that particles can be stabilized in solution by structured solvent surrounding the particles.⁹⁰ This couples to the nanostructure in the ionic liquid to create alternating layers of anions and cations that are known as solvation layers. Such ionic ordering of the solvent propagates some distance into the ionic liquid and provides repulsive force acting between two particle surfaces dispersed in the ionic liquid. The oscillating distant-dependent solvation forces have

been observed between macroscopic mica and silica surfaces in both protic and aprotic ionic liquids by surface force measurements as shown in Figure 1.5,¹⁰³⁻¹⁰⁸ which are consistent with molecular dynamics simulation.¹⁰⁹ Discrete friction across ionic liquid thin films between two mica sheets have been discovered to be a function of surface separation distance or integer number of ion layers in the film. These measurements and simulations indicate that the ion pairs are arranged in a layered structure near the solid surfaces.¹⁰⁷

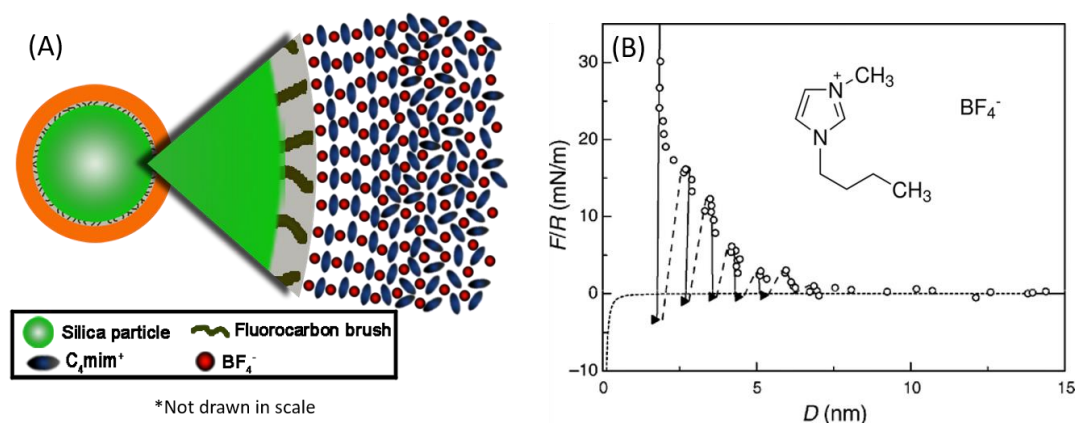


Figure 1.5: (A) Schematic illustration of the structured solvent around fluorinated coated silica nanoparticle in ionic liquid [C₄mim][BF₄]. This structured solvent is initiated by the hydrogen bonding between coated fluorocarbon chains and [BF₄]⁻ anion groups. Cations form cations layers around anion through ionic bonds and this ordered layer structure gradually becomes disordered when away from the surface of particles. (B) Solvation force between two macroscopic silica surfaces in [C₄mim][BF₄]: Normal force scaled with surface curvature radius (F/R) as a function of surface separation D . Dotted lines represent van der Waals attractions calculated from Lifshitz theory. Solid and dashed lines in plots indicate stable and unstable regions, respectively. Part (A) is adapted with permission from Gao J., et al. *ACS Nano* 2015, 9, (3), 3243-3253. Copyright 2015 American Chemical Society; Part (B) is adapted with permission from Ueno, K., et al. *Phys. Chem. Chem. Phys.* 2010, 12, 4066-4071. Copyright 2010 The Royal Society of Chemistry.

Besides the solvation layering, the suspension stability in ionic liquids can be achieved by polymer grafting to the particle surface when IL is a good solvent for the polymer.^{96, 110} Poly(methyl methacrylate) (PMMA) is soluble in 1-butyl-3-methylimidazolium hexafluorophosphate ([C₄mim][PF₆]) and 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C_nmim][NTf₂]), the PMMA-grafted silica nanoparticles were reported to show good dispersion in these two ionic liquids. However, such coated particles show poor dispersion if PMMA is insoluble in other ionic liquids (*e.g.*, [C₄mim][BF₄]).⁹⁶ Such particle stability is mainly a result of the compatibility of solvent with coated polymer chains, which can be controlled by tuning the solvent quality through pH,⁷¹ temperature,^{62, 110} *etc.* The mechanism of such particle stability is afforded by the steric repulsion between the grafted layers and is system dependent, *i.e.*, the system will become unstable when the brush is immersed into a poor solvent and collapses.¹¹¹ The stability provided by surface grafted polymers through steric repulsion is reported to be thermal-sensitive and a temperature-induced colloidal glass-to-gel transition was observed.^{62, 110} However, such polymer-stabilized dispersions do not exhibit shear thickening rheology in the regimes studied presumably due to the strong nanoscale repulsive forces afforded by the well-solvated polymer brush.¹¹²⁻¹¹³

1.5 Shear Thickening Fluid (STF) – ArmorTM

The ability of STFs to behave as a liquid or solid under different shear rate or shear stress can be beneficial for applications where rate-sensitive behavior or energy adsorption is critical. STFs have been used as an additive material and impregnated into protective fabrics, such as Kevlar[®], to improve the performance of regular body armor made by Kevlar[®] fabric.¹⁵ The scanning electron microscopy (SEM) images of

the treated STF-Kevlar[®] material are shown in Figure 1.6.¹⁴ It can be found that the STF fully wets the fabric, penetrating between fibers within a yarn. As the size of the silica particles are much smaller than the diameter of the Kevlar[®] fiber, the STF can be treated as a continuum relative to the fabric.

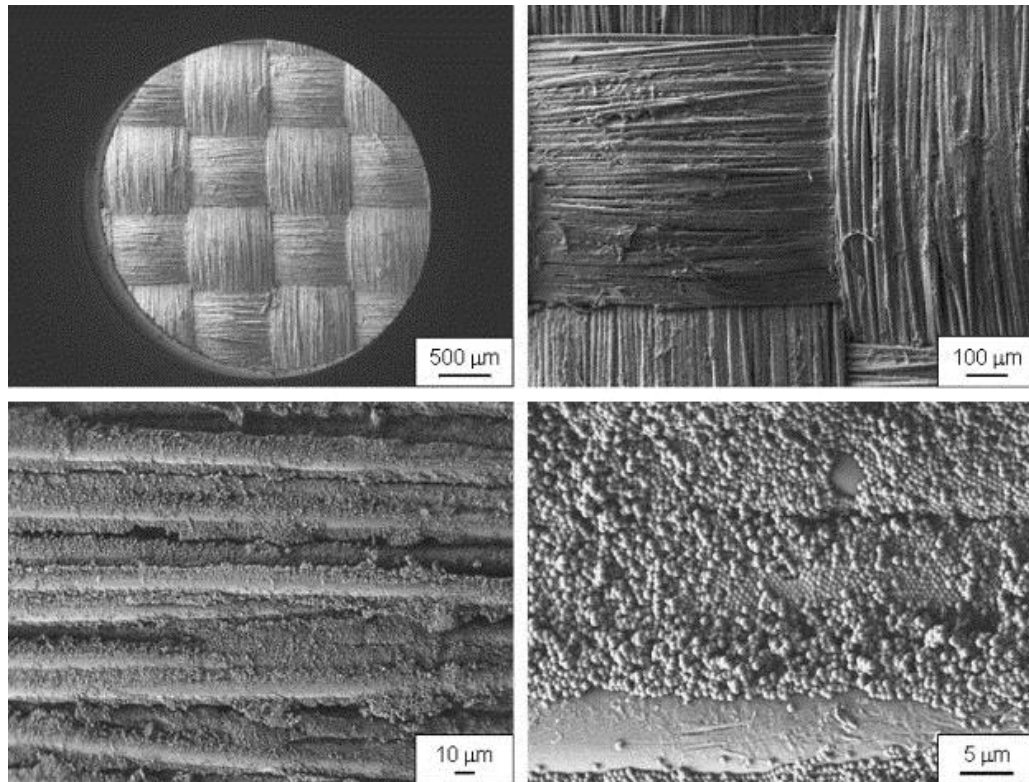


Figure 1.6: SEM images of woven Kevlar[®] impregnated with STF between fibers. Adapted with permission from Decker, M., *et al.* Composites Science and Technology 2007, 67 (3), 565-578. Copyright 2007 Elsevier.

This enhanced protective nanocomposite material after intercalated with STF are often referred as STF-Armor[™], which can be used for ballistic, puncture, and blast protection for the military, police, and first responders. The STF-Armor[™] is as

flexible as the bare Kevlar[®] fabric because STF has liquid-like properties at the shear rates associated with normal movements. When impacted by a bullet or fragment traveling at high speed, the STF rigidizes almost instantaneously to aid in stopping the projectiles. STF enhances the performance of Kevlar[®] by restricting the relative movement of adjacent fibers when impacted, thereby taking full advantage of the high tensile strength of Kevlar[®].¹¹⁴⁻¹¹⁷ Additionally, it has been shown that the STF can distribute stress away from the impact site to neighboring fibers, engaging a larger portion of the fabric in energy absorption. STF-nanocomposites have been proven to provide enhanced protection against puncture and ballistic threats which would otherwise easily penetrate the bare Kevlar[®] with the same or reduced mass and more flexibility than conventional materials.^{14, 117} Figure 1.7 demonstrates one example of the superior puncture resistance of STF-ArmorTM nanocomposites as compared to conventional Kevlar[®].¹⁴ STF-Kevlar[®] exhibits significantly better stab resistance with less layer penetration and higher energy dissipation as compared with the neat Kevlar[®] of equal areal density. Furthermore, neat Kevlar[®] shows significant puncture damage, while there is little obvious damage to the STF-Kevlar[®].

Besides the superior protection against puncture and ballistic threats, STF-ArmorTM have been shown to provide enhanced protection against simulated hypervelocity MMOD impacts, which occurs with extreme high energy and short time scale.⁵ With the neoprene-coated nylon absorber layers of the standard thermal micrometeoroid garment (TMG) are substituted with STF-ArmorTM, the prototype lay-ups provide meaningful hypervelocity impact protection from MMOD threats with higher energy absorption.

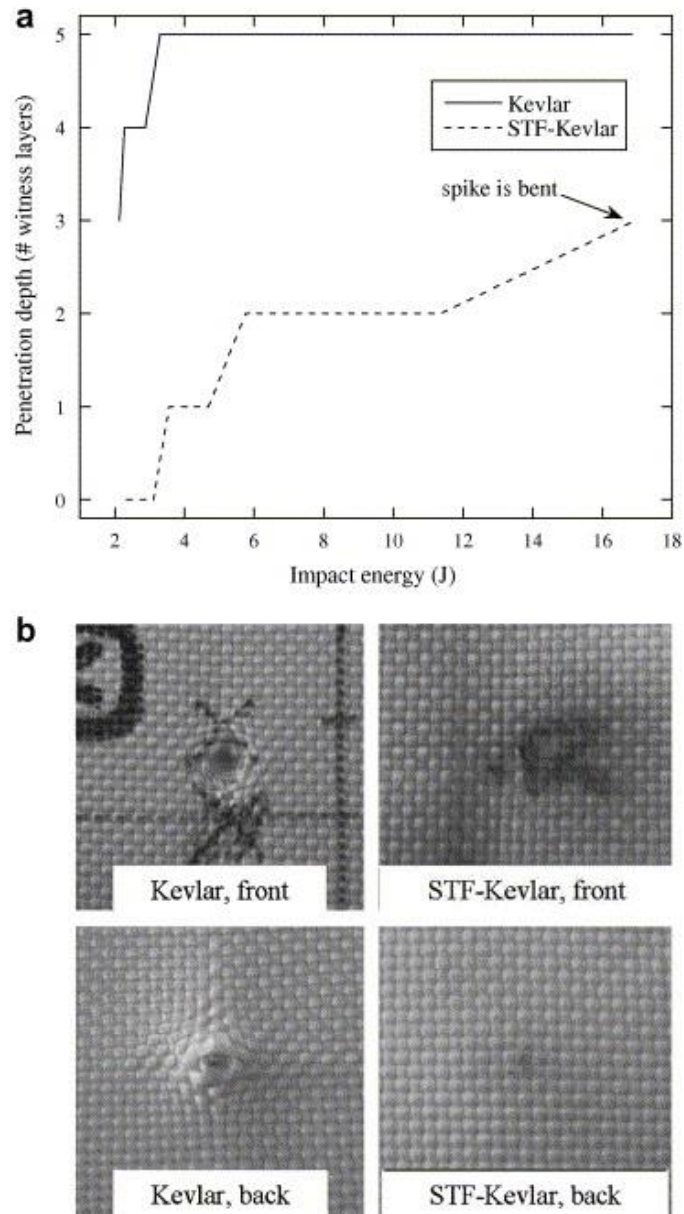


Figure 1.7: (a) Results of National Institute of Justice (NIJ) 0115.0 spike stab resistance test for body armor on 15 layers of neat Kevlar[®] (270 g/) and 12 layers of STF-Kevlar[®] (271 g/). The plot shows the number of witness papers placed behind the target that are penetrated. Penetration of all 5 layers indicates failure. (b) photographs of Kevlar[®] and STF-Kevlar[®] fabric damage after NIJ 0115.0 spike puncture test at $m = 2.33$ kg and $h = 0.75$ m. Adapted with permission from Decker, M., *et al.* Composites Science and Technology 2007, 67 (3), 565-578. Copyright 2007 Elsevier.

1.6 Thesis Objectives and Overview

This dissertation has three goals. The primary goal of my dissertation is to develop shear thickening fluid formulations that are stable under simulated space conditions and to intercalate them with aramid fabrics Kevlar[®] to formulate STF nanocomposites that are appropriate for space applications. Materials made for the environment of low earth orbit must be able to withstand vacuum and extreme temperatures.¹¹⁸ An STF formulation for space applications requires a carrier medium that will remain flowable under vacuum and extreme low temperatures. However, the shear thickening fluid formulations of the current generation of multi-threat protective composites use polyethylene glycol as the carrier medium, which will solidify at low temperature and evaporate under vacuum. Thus, ionic liquids are chosen due to their low volatility and thermal stability especially under low temperature, which will meet the formulation requirements.¹¹⁹

Unfortunately, to date, there have been only a few literature reports of shear thickening colloidal dispersions formulated in ionic liquids.^{96, 110} Colloidal particles are reported to aggregate in ionic liquids due to the screened electrostatic repulsion under high ionic strength. Consequently, research into the mechanisms by which particles can be dispersed into ionic liquids such that shear thickening rheology can be achieved is warranted. To address this in part, the second goal of this dissertation is to study the nanostructure, stability, and dynamics of model, surface-functionalized spherical silica particles in a common aprotic ionic liquid [C₄mim][BF₄]. Direct measurements of surface structure around nanoparticles and a predictive, quantitative knowledge of inter-particle interactions in ionic liquids will be crucial to predict and control colloidal stability in ionic liquids. With these knowledge, the desired shear

thickening response and transition rate and strength will be achieved by controlling the structure on the particle surface through engineering particle phase chemistry.

In order to successfully complete the first and second goals, the rheology of ionic liquid colloidal dispersions needs to be accurately measured. However, water is a common contaminant in ionic liquids due to their hygroscopic nature,⁶⁷ especially for hydrophilic ionic liquids. Furthermore, ionic liquids can easily absorb water from atmospherically humidity during the rheological measurement in lab, affecting the measured viscosity and microstructure. Thus, it is crucial to understand the interaction between water molecules and ionic liquids. The last goal of this dissertation is to study this water-ionic liquid interaction and any changes in microstructure cover the whole composition range.

The structure of this dissertation is organized as follows. Chapter 2 outlines the relevant experimental techniques used in this dissertation. Chapter 3 presents a study on the effect of addition of water molecules on the physical properties (density and viscosity) and microstructure of an ionic liquid [C₄mim][BF₄]. The phase transition of ionic liquid [C₄mim][BF₄]-water mixtures covering the full composition range from high salt to low salt is investigated. Densities, viscosities and their semi-empirical correlation of the homogenous binary mixtures of [C₄mim][BF₄] with water are reported for a wide temperature range. This study provides a guidance on the rheological measurements for the rest of this dissertation. Chapter 4 describes the materials and the protocol used to synthesize fluorocarbon coated silica particles, which will be used and further discussed in Chapter 5. The particle properties, such as the chemical coating, particle size, and density, are evaluated. Chapter 5 demonstrates the critical role of solvation forces in dispersing and stabilizing nanoparticles and

colloids in $[\text{C}_4\text{mim}][\text{BF}_4]$. A stable dispersion of solid silica nanoparticles in ionic liquid $[\text{C}_4\text{mim}][\text{BF}_4]$ is achieved by particle surface chemical functionalization with a fluorinated alcohol. In Chapter 6, a successful attempt to formulate stable nanoparticle dispersions in ionic liquids that exhibit significant shear thickening through designing the surface coating of particles (alcohol coating) is described. Their rheological response to temperature is investigated and interpreted in terms of particle interactions and interfacial structure. With the successful development of a shear thickening fluid formulation with strong shear thickening strength, the new ionic liquid based formulation is intercalated with Kevlar[®] and the penetration resistance of the ionic liquids based STFs- Kevlar[®] nanocomposites are described in Chapter 7. The effect of changing from the traditional STF carrier medium, PEG, to ionic liquid $[\text{C}_4\text{mim}][\text{BF}_4]$ has been studied. Optimal areal density, penetration peak force, and dissipated energy are obtained through design of the treatment condition. Chapter 8 summarizes the major conclusions of this dissertation and identifies directions for future work.

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Chapter 2

EXPERIMENTAL METHODS

In this chapter, an overview of the experimental methods and techniques used throughout this dissertation is described. Unless otherwise stated, experiments are conducted and results are analyzed according to the procedures described herein. These methods include dynamic light scattering (DLS), scanning/transmission electron microscopy, densitometry, thermogravimetric analysis (TGA), rheological characterization, small angle neutron scattering (SANS), X-ray scattering, and quasi-static puncture test on textile materials. The designed vacuum cell setup, which is used to measure the rheological response of shear thickening fluids (STFs) under simulated space vacuum condition, is described in Section 2.6.3, and the primary results are discussed in Chapter 9. Materials and sample preparations are outlined in the “Materials and Methods” Section of the corresponding chapter.

2.1 Dynamic Light Scattering (DLS)

The effective hydrodynamic size and the size distribution of particles are evaluated by DLS through measuring the diffusion coefficient of the particles in dilute suspension undergoing Brownian motion.

In a typical measurement, a monochromatic light source, usually a laser, is projected through a polarizer and into a sample cell. The diffracted light from all of the particles can either interfere constructively or destructively. The interaction between the incident beam and the random Brownian motion of the particles in the

liquid sample causes random fluctuations of intensity as a function of time. The intensity autocorrelation function is recorded as a function of time, given by¹⁻²

$$G_2(q, \tau) = \frac{\langle I(q, t) I(q, t + \tau) \rangle}{\langle I(q, t) \rangle^2} \quad 2-1$$

$$q = \frac{4\pi n_0}{\lambda} \sin\left(\frac{\theta}{2}\right), \quad 2-2$$

where $G_2(q, \tau)$ is the intensity autocorrelation function, q is the momentum transfer vector, τ is the delay time, $I(q, t)$ is the scattering intensity at the scattering vector q and time t , n_0 is the refractive index of the sample, λ is the wavelength of the laser, and θ is the angle of the photodetector. The autocorrelation function $G_2(q, \tau)$ can be converted to the first-order autocorrelation function $G_1(q, \tau)$ through the Siegert relation as shown below¹

$$G_2(q, \tau) = B_0 + \xi |G_1(q, \tau)|^2, \quad 2-3$$

where B_0 is the baseline, which is close to unity, and ξ is the instrument parameter, usually is on the order of 0.1-1 and is close to unity for an optimum experiment.

Analysis of the intensity correlation function is performed using the cumulant method,^{1, 3}

$$G_1(q, \tau) = \exp(-\Gamma \tau) \left(1 + \frac{\sigma}{2} \tau^2 + \dots\right), \quad 2-4$$

where Γ is the average decay rate, which characterizes the average relaxation time of the particle, and σ is the coefficient of variation, which gives the polydispersity index of the sample. Through a non-linear fitting to the intensity decay data using Equation 2-4, the average decay rate Γ and the coefficient of variation σ are obtained.

For spherical particle system, the average decay rate Γ is related to the diffusion coefficient D by

$$\Gamma = q^2 D. \quad 2-5$$

The hydrodynamic radius R_H of the particles is then calculated from the Stokes-Einstein-Sutherland relation^{2, 4}

$$D = \frac{k_B T}{6\pi\mu R_H}, \quad 2-6$$

where μ is the viscosity of the solvent, k_B is Boltzmann's constant, which is 1.38×10^{-23} J/K, and T is the absolute temperature. The polydispersity index (PDI) is calculated from the average decay rate Γ and the coefficient of variation σ by¹

$$PDI = \frac{\sigma}{\Gamma^2}. \quad 2-7$$

Herein, the DLS measurements were performed on a ZetaPALS instrument (Brookhaven Instruments). The instrument optimized the power of the incident laser at the beginning of each measurement with an incident photon wavelength $\lambda = 658$ nm. The scattered light intensity was recorded by a photodetector at a scattering angle $\theta = 90^\circ$. For the system investigated in this dissertation, $q = 0.025 \text{ nm}^{-1}$, and $n_0 \sim 1.4$ (e.g., [C₄mim][BF₄], $n_0 = 1.42$, silica dioxide, $n_0 = 1.46$). The auto-correlation function was measured over a period of 120 s and the average decay time was extracted by fitting to a second-order cumulant expansion using the ZetaPALS software.

Prior to the DLS measurements, the instrument was warmed up for 30 min, allowing it to equilibrate to the experimental temperature and stabilize the laser. The cuvette cells were rinsed by ethanol followed by compressed air to dry the surface. All the raw materials were filtered by a 0.2 μm Nalgene syringe filter when preparing

samples, no further filtration performed on the final sample before loading into the cuvette cell. On each DLS measurement, 10 repeated data collections were carried out with each spanned 2 mins in order to get a good statistical average value and standard error. Number-averaged particle size and polydispersity were extracted from the software analysis.

2.2 Scanning/Transmission Electron Microscopy (SEM, TEM)

Advanced microscopy techniques such as SEM and TEM are essential techniques to investigate the microstructure, morphology, particle size, and particle coatings of the sample. SEM produces images of a sample surface by raster scanning it with a focused beam of electrons. Through collecting the secondary electrons emitted by the atoms excited by the electron beam, an image displaying the topography of the surface is generated. TEM is a microscopy technique in which a beam of electrons is transmitted through an ultra-thin specimen, interacting with the specimen as it passes through it. The difference of the electron densities between the specimen and its background enables imaging.

In this dissertation, a high resolution SEM (JEOL JSM-7400F) was used to capture the dried silica particles, and their size distributions were analyzed through ImageJ software.⁵ Samples were prepared on aluminum stubs (Electron Microscopy Sciences) with an adhesive carbon tab (Electron Microscopy Sciences). A dilute suspension of silica particles was pipetted onto the aluminum stubs, and dried by atmosphere air. Then the dried samples were sputter-coated with an Au/Pd layer under vacuum for 40 s to increase their conductivity. After that, the samples were loaded into the SEM chamber and digital images were recorded.

TEM images of the nanoparticles were taken on a JEOL JEM-2000FX (LaB6) TEM operated at 200 kV. A droplet of the fluorocarbon-coated particle/ethanol solution was dispensed onto a carbon-sputtered copper grid, and the grid was loaded into the TEM chamber after the ethanol completely evaporated. High resolution TEM images then were recorded. The fluorinated particles dispersed in [C₄mim][BF₄] were imaged directly in their solution phase. Samples were prepared by placing a small droplet of dilute particle/[C₄mim][BF₄] dispersion onto a carbon-sputtered copper grid. Extra solution was removed by blotting with filter paper, leaving a thin film of dispersion on the grid. Liquid nitrogen was constantly supplied during the experiment to eliminate static electricity which could blur the micrographs.

2.3 Densitometry

Gravimetric densitometry is used to determine the density of the liquid samples (such as suspensions and aqueous solutions). The sample is introduced into a U-shaped glass tube which is being excited to vibrate at its characteristic frequency. Through oscillating the U-tube, a correlation between the oscillation frequency and the density of the sample enables the determination of the density of the liquid sample.

The skeletal density of particle in solution is estimated based on the densities of a series of dilute particle suspensions with particle mass fraction $0 \leq x < 0.02$. Assuming ideal mixing of the dispersion constituents, the particle density can be extracted using the following equation:

$$\frac{1}{\rho_{\text{solution}}} = \left(\frac{1}{\rho_{\text{particles}}} - \frac{1}{\rho_{\text{solvent}}} \right) x + \frac{1}{\rho_{\text{solvent}}}, \quad 2-8$$

where, ρ_{solution} , $\rho_{\text{particles}}$, and ρ_{solvent} are the density of the solution, particle, and solvent, respectively; x is the mass fraction of particles in solution.

Measurements of the particle dispersions densities and solution mixtures at atmospheric pressure were conducted on an Anton Paar DMA-4500M densitometer. The temperature of the sample inside the U-shaped glass tube is controlled within the range of 10 °C to 90 °C by a Peltier temperature control system (accuracy of ± 0.03 °C). The accuracy of the measured density is reported to be $\pm 5 \times 10^{-5}$ g/cm³ by the instrument. The densitometer was calibrated with dry air and ultra-pure water at atmospheric pressure before each measurement. For density measurements, a liquid sample was injected into the U-shaped glass tube using a 3 mL syringe slowly to eliminate the formation of air bubble inside the sample. The temperature of the sample was equilibrated for at least 5 minutes at set temperature before taking measurement, thus minimizing the effect of temperature fluctuation on the oscillation of U-tube. Between each measurement, the U-shaped glass tube was flushed with excess solvents (water, ethanol, and soapy water) gently and then dried by an air fan. “Air check” and “water check” were performed after cleaning to ensure no sample residual in the U-tube, which otherwise would have significant influence on the density measurement.

2.4 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis is a method of thermal analysis in which the mass of a substance is monitored as a function of temperature or time as the sample specimen is subjected to a controlled temperature program in a controlled atmosphere.⁶ TGA is commonly used to determine selected characteristics of materials that exhibit either mass loss or gain due to decomposition, oxidation, or loss of volatiles.

In this dissertation, TGA is applied to evaluate the decomposition of surface coating of silica particle, from which the grafting density of coated fluorocarbon can be derived. The TGA instrument continuously weighs a sample as it is heated in a furnace. During a heating experiment, various components of the sample are decomposed as the temperature goes up, and the weight percentage of each resulting mass change can be measured. Results are displayed with temperature on the X-axis and mass loss on the Y-axis. The relative weight fraction of different components can be calculated based on the transition temperature during experiment and the material's specific combustion temperature. For example, the decomposition temperature of fluorocarbon 1H,1H,9H hexadecafluoro-1-nonanol is ~ 300 °C, while the melting temperature of the silica core is over 2000 °C. Because of the large difference between the combustion temperature of the grafted fluorocarbon chain and the silica particle core, the decomposition signal of fluorocarbon can be easily distinguished. The grafting density of the fluorocarbon on the surface of silica particles, which is the number of fluorocarbon chain per nm^2 of the particle surface, can be readily obtained.

In this thesis work, TGA measurements were performed using a TA Instruments Q500. Two samples: dried uncoated silica particle and fluorocarbon coated silica particle were tested. Prior to the TGA measurement, both of the uncoated and coated silica particles were dried under a stream of nitrogen gas for 5 hours and then in a vacuum oven for 24 hours; however, there was still physically adsorbed water residual left in the pores of the particle. Thus, the physical absorbed water needs to be considered when designing the temperature heated-up program. Specifically, the temperature was increased from 25 °C to 80 °C at a rate of 10 °C/min and equilibrated at 80 °C for 20 min to remove physically adsorbed water. Then, the

temperature was increased to 900 °C at the same rate as before and equilibrated at 900 °C for 15 min to ensure complete decomposition of coated fluorocarbon. Nitrogen gas was flowing through the sample pan over the entire measurement. By comparing the final mass loss of uncoated and coated silica particles, the grafting density of fluorocarbon can be deduced.

2.5 Rheological Characterization

2.5.1 Falling-Ball Viscometry

The falling-ball viscometer typically measures the viscosity of gases and Newtonian liquids of low viscosity. A falling-ball viscometer has a spherical ball falling down along a tube containing the sample liquid to be measured. The temperature of sample is controlled by a concentrically surrounded tubular jacket. Newton's law of motion is applied to the force balance of a falling sphere ball when it reaches its terminal steady velocity,⁷ that is a ball falling under the force of gravity in a fluid attains a terminal steady velocity when the net force of frictional (drag) force, gravity force, and buoyancy force reaches zero, such that

$$F_D + F_B = m_s g , \quad 2-9$$

where m_s is the weight of spherical ball, F_B is the buoyancy force, and F_D is the drag force. In the case of a boundless fluid medium and a negligible inertial effect (Reynolds number $Re \ll 1$), the drag force F_D can be obtained from Stokes' law,⁷⁻⁸

$$Re = \frac{\rho_f V d}{\mu} \quad 2-10$$

$$F_D = 3\pi\mu V d , \quad 2-11$$

where ρ_f is the density of the measured fluid sample, V is the terminal velocity of the falling ball, d is the diameter of the falling ball, μ is the viscosity of the measured fluid. Thus, the force balance becomes:

$$3\pi\mu Vd + \left(\frac{\pi d^3}{6}\right)\rho_f = \left(\frac{\pi d^3}{6}\right)\rho_s. \quad 2-12$$

From this equation, the viscosity of fluid sample can be determined when the density difference between the spherical ball and the measured fluid, the diameter and terminal velocity of the spherical ball are known, yielding

$$\mu = \frac{(\rho_s - \rho_f)d^2}{18V}. \quad 2-13$$

Equation 2-13 can be simplified to the following form:

$$\mu = K(\rho_s - \rho_f)t \text{ where } K = \frac{gd^2}{18l}. \quad 2-14$$

In this equation, t is the time needed for the spherical ball to pass the falling length l .

In this dissertation, the dynamic viscosities of ionic liquid and the mixture with water solutions were measured using an Anton Paar AMVn automated microviscometer at temperatures from 20 °C to 100 °C under atmospheric pressure condition. The temperature was controlled by a built-in Peltier thermometer with an accuracy of 0.05 K. The time t_0 of a ball falling over a defined distance in a capillary is determined by a laser detector. As the glass capillary tube is displaying at an angle $<90^\circ$ instead of vertical, Equation 2-14 can be modified to yield

$$\mu = K(\alpha)(\rho_s - \rho_f)t_0. \quad 2-15$$

Where $K(\alpha)$ is the calibration constant of the measuring system at α angle.

Measurements were conducted at three different angles using calibrated capillary tube

($d = 3.0$ mm) and stainless steel balls ($d = 2.5$ mm) following standard protocols,⁹ and for each angle measurements were repeated four times. The instrument accuracy for time is reported to be 0.002 s.

2.5.2 Rotational Rheometry

Rheological measurements were conducted on two types of rheometers in this dissertation: an AR-G2 Rheometer and a Discovery Hybrid Rheometer (DHR) from TA Instruments. Both of them are stress controlled rheometers with Peltier plate temperature control within 0.01 °C. Their magnetic drive motor and optical encoder are located in the head of the rheometer as shown in Figure 2.1B. As ionic liquid [C₄mim][BF₄] corrodes aluminum coating at high temperature, stainless steel tools were used for rheological measurements. Moreover, cone and plate geometry was used to ensure homogeneous shear rate (Figure 2.1A). Conversion between the applied and the measured parameters (torque M and strain γ) and the rheological material functions were processed using the TA Instruments Trios software. To erase any previous shear histories and maintain a consistency between measurements, a steady pre-shear was applied at a shear stress of 10 Pa for 2 min prior to each dynamic rheological measurement. Two standard shear experiments: steady shear and oscillatory shear rheometry were used in this dissertation.

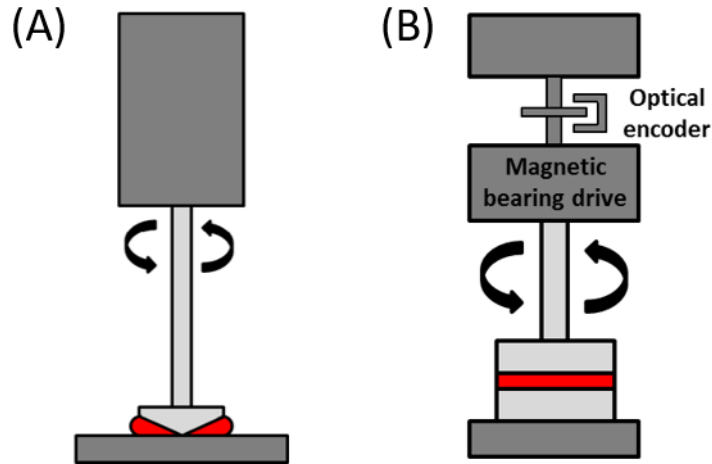


Figure 2.1: Schematics of (A) the cone and plate geometry with sample (marked in red color) and (B) stress-controlled AR-G2/DHR rheometer from TA Instruments.

2.5.2.1 Steady Shear Measurements

Steady shear measurements were employed to evaluate the shear viscosity of materials at different shear stress/shear rate. Cone and plate geometry (40 mm stainless steel cone with 2° cone angle) was applied with homogeneous shear rate throughout the radius of cone geometry. The shear rate $\dot{\gamma}$ is given by

$$\dot{\gamma} = \frac{\Omega}{\beta} , \quad 2-16$$

where Ω is the angular velocity, and β is the cone angle in radians.

For the steady shear tests, a series of steady flow sweeps were performed. The flow sweeps were always conducted by increasing stress first followed by decreasing stress. Multiple forward and backward sweeps were performed to check for hysteresis. At each shear stress, during steady flow sweep, the sample was equilibrated at this stress for 5 seconds, and then the viscosity value was measured for a duration of 60

seconds. Peak hold tests, constant shear stress or shear rate for a period of time, were conducted at certain shear stresses to ensure a true steady state was reached during the flow sweep measurements.

2.5.2.2 Small-Amplitude Oscillatory Shear (SAOS) Measurements

As depicted in Figure 2.2, in a small amplitude oscillatory shear measurement, a sinusoidal strain $\gamma(t)$ or shear rate $\dot{\gamma}(t)$ at an oscillatory frequency ω is applied to a sample, and the responsive sinusoidal stress is measured:¹⁰

$$\gamma(t) = \gamma_0 \sin(\omega t) \quad 2-17$$

$$\dot{\gamma}(t) = \gamma_0 \omega \cos(\omega t) \quad 2-18$$

$$\sigma(t) = G^* \gamma_0 \sin(\omega t), \quad 2-19$$

where t is the time, γ_0 is the maximum strain, $G^*=(G'+iG'')$ is the viscoelastic complex modulus.¹⁰⁻¹¹ The linear viscoelastic storage /elastic (G') represents the elasticity of the material, and the loss/viscous moduli (G'') characterizes the ability of a material to dissipate energy. They are defined as

$$\sigma(t) = (G'(\omega) + iG''(\omega))\gamma(t) \quad 2-20$$

$$G'(\omega) = \frac{\sigma_0}{\gamma_0} \cos \delta \quad 2-21$$

$$G''(\omega) = \frac{\sigma_0}{\gamma_0} \sin \delta, \quad 2-22$$

where δ is the phase angle (the phase difference between the stress and the strain). δ is 0° and 90° for perfect elastic solids and viscous liquids, respectively. The phase angle δ is defined as the ratio of the viscoelastic moduli, and is a useful parameter to quantify the elasticity of a material:

$$\tan(\delta) = \frac{G''(\omega)}{G'(\omega)} . \quad 2-23$$

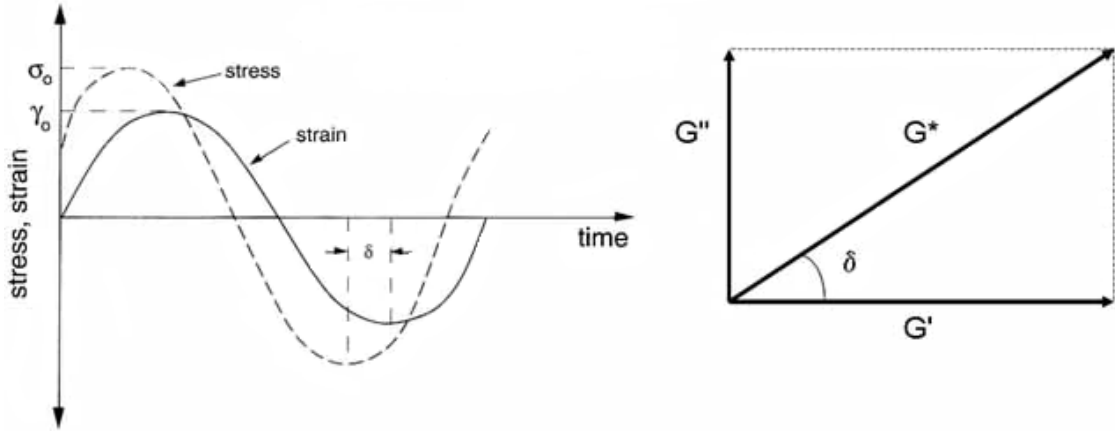


Figure 2.2: Example of strain deformation, the linear stress response, and phase shift as a function of time in a small amplitude oscillatory shear experiment.

A strain sweep is utilized to determine the linear viscoelastic regime (LVE) for each sample, where G' and G'' are independent on the strain applied, before frequency sweep tests. As the LVE changes with temperature, strain sweep measurements need to be conducted for each temperature at interest. In the following frequency sweep measurements, an oscillatory strain, which is sufficiently large to perturb a sample without disturbing the structure of the sample at equilibrium state, is chosen in the linear regime. For the time-temperature superposition measurement, the sample was equilibrated at target temperature for at least 10 min to ensure a homogenous temperature profile inside the sample.

2.5.3 Pressure/Vacuum Cell Geometry

In this dissertation, a vacuum cell was developed based on the pressure cell provided by TA Instruments and it has been used to study the rheology of ionic liquid based shear thickening fluids under vacuum condition. The vacuum cell setup is shown in Figure 2.3. Turbomolecular pump station (HiCube™ 80 Eco from Pfeiffer Vacuum) is connected to the vacuum cell through flexible stainless steel tubes. The pressure inside the vacuum cell can reach 1×10^{-6} torr within one hour, which is monitored by a Full Range® Complete Pressure Gauge PKR361.

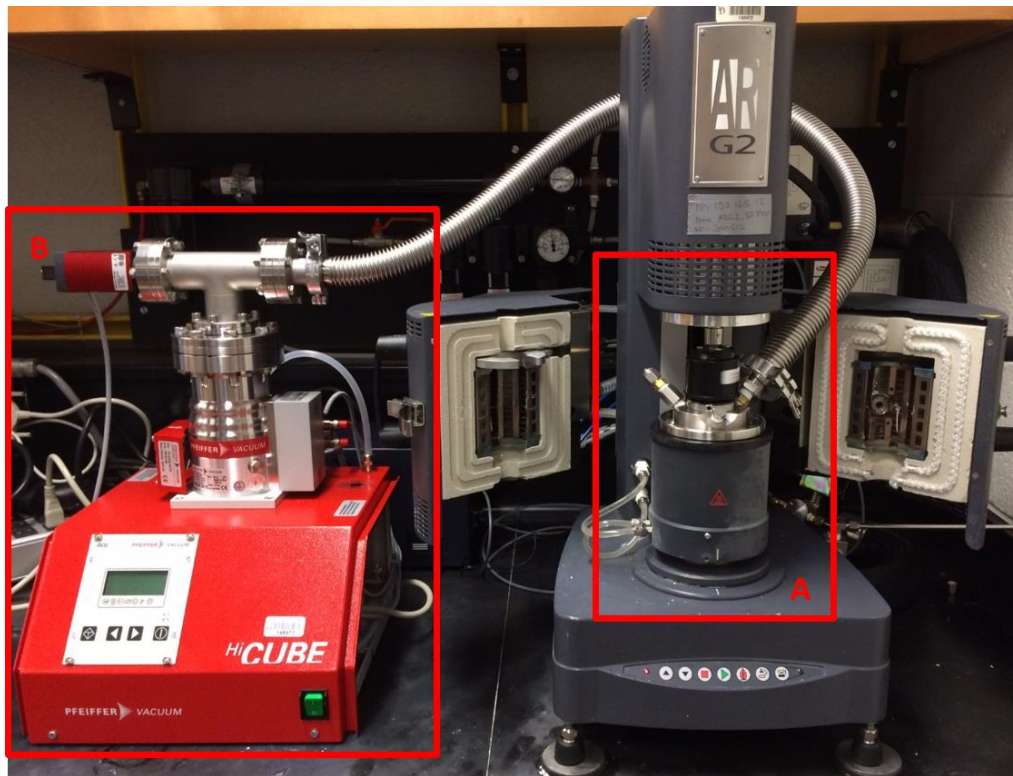


Figure 2.3: The vacuum cell setup for rheological test on ionic liquid based STFs under simulated space vacuum condition. (A) Vacuum cell on the AR-G2 rheometer to measure the rheological response; (B) Turbomolecular pump station to reduce the pressure inside the vacuum cell to 10^{-6} torr.

The vacuum cell has a standard concentric cylinder geometry, with temperature controlled by a Peltier-controlled heating jacket (-10 °C to 300 °C). A copper sheath is fitted to the cell to ensure good heat transfer between the jacket and the cell. The cell consists of three main component assemblies, including the cell cup, the concentric cylinder rotor, and the magnet assembly as shown in Figure 2.4. The rotor assembly contains the concentric cylinder rotor, which is mounted on a shaft attaching to a four-pole magnet located under the rotor assembly cap, as shown in Figure 2.5. The cell cup contains the sample fluid and is inserted into the Peltier jacket. The inner radius of the cup is 14.00 mm, the outer radius of the rotor is 13.00 mm, and 9.5 ± 0.5 mL volume of sample is needed for each test. The magnet assembly is attached to the rheometer's rotating spindle, and then it is brought down over the rotor assembly. The measured fluid samples are sealed inside the cell cup. Samples are sheared by the rotor inside the cell, which is controlled by the magnet assembly through magnetic force. The stress-strain response is recorded and analyzed using Trios software.

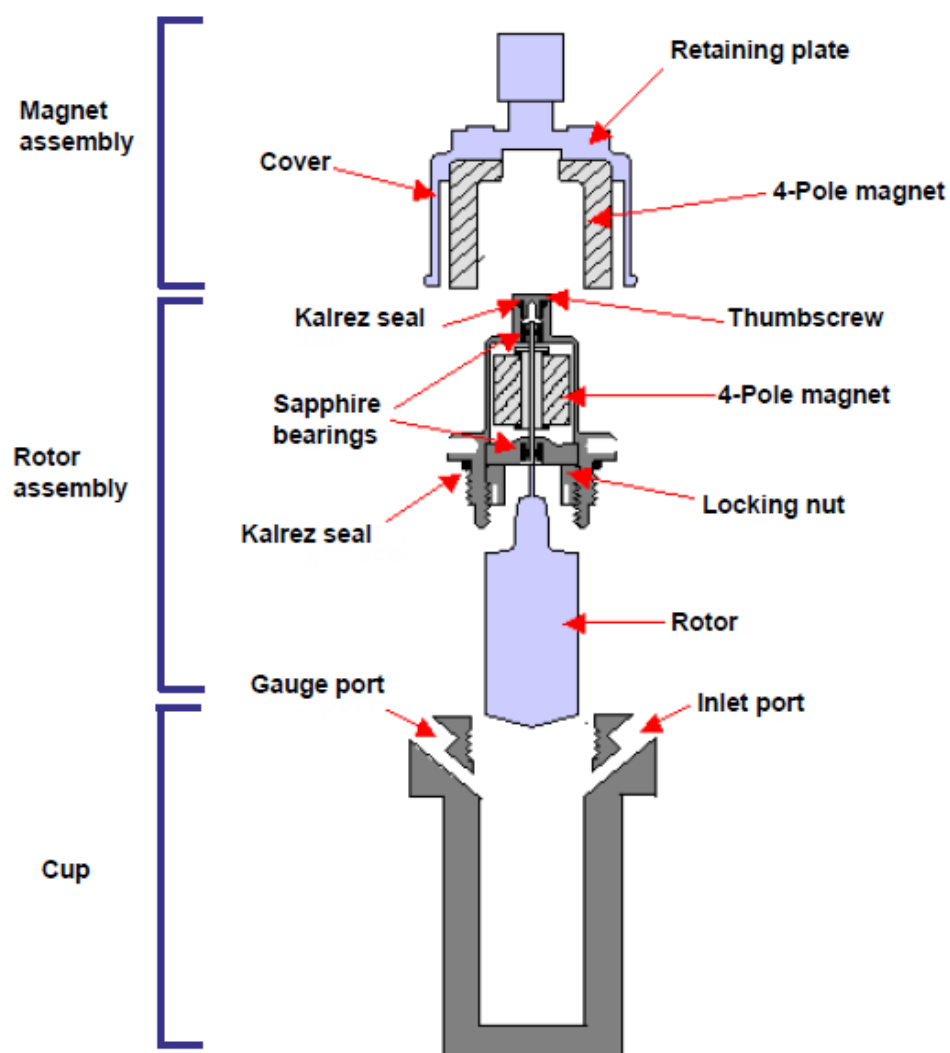


Figure 2.4: Cross-section schematic of vacuum/pressure cell.¹²

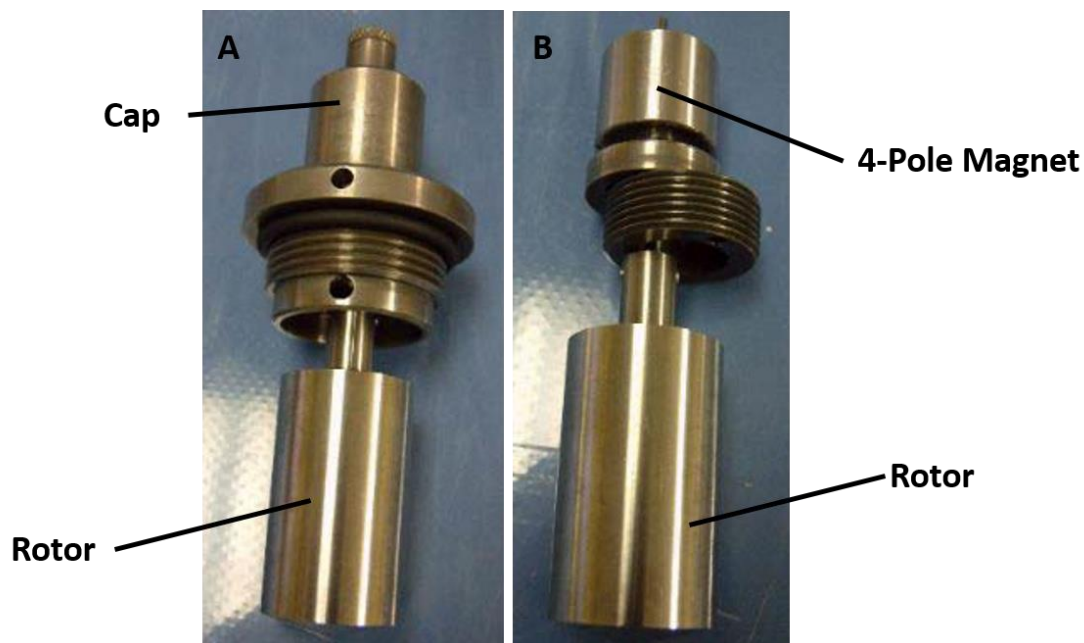


Figure 2.5: Pressure cell rotor assembly with cap on (A) and off (B).¹²

2.6 Small-Angle Neutron Scattering (SANS)

Small angle neutron scattering is a well-established characterization technique and has been widely applied to investigate the microstructure of various materials. Hence, SANS is employed to study the microstructure of ionic liquid aqueous solutions and silica particle-ionic liquid colloidal suspensions. The quiescent microstructures of the complex fluids are investigated using static SANS, whereas their microstructures induced by shear flow are studied by rheo-SANS and flow-SANS.

A schematic illustration of SANS is shown in Figure 2.6. A defined incident neutron beam of wavelength λ passes through a sample, interacts with the sample, giving a wave vector q at a scattering angle θ , which is defined as

$$q = |\vec{q}| = |\vec{k}_s - \vec{k}_i| = \frac{4\pi}{\lambda} \sin\left(\frac{\theta}{2}\right). \quad 2-24$$

Intuitively, a measurement made at a given q allows to investigate the density fluctuations in the sample on a distance scale $D = 2\pi/q$. With neutrons of a typical wavelength of 6 Å, the length scale probed by SANS measurements is O(1-100 nm) depends on the geometry configurations. This covers the range of structure (micellar, emulsion, and particle) discussed in this dissertation. More than 10^5 scattering counts are recorded for each single SANS measurement to obtain good statistics when analyzing the results.

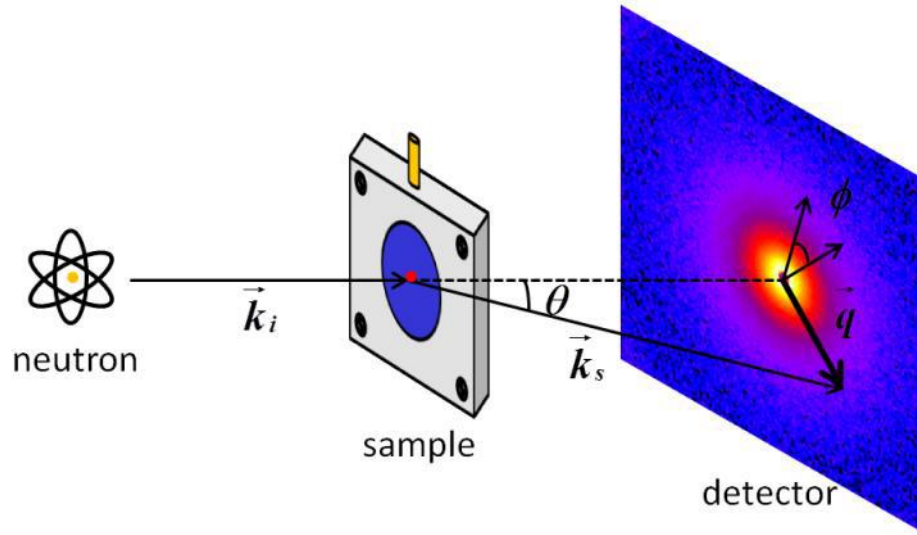


Figure 2.6: Illustration of a typical SANS experiment.

For the SANS measurement, the scattering intensity is related to the structure and the scattering length density (SLD) distribution of the sample. Assuming the

coherent scattered intensity measured by SANS is equal to the scattering cross-section, the total scattering intensity is given by:

$$I(q, \phi) = n_p P(q, \phi) S(q, \phi) + I_b, \quad 2-25$$

where n_p is the number density of the scattering objects, and I_b is the intensity of incoherent scattering background. $P(q, \phi)$ is the form factor, which describes the scattering from individual particle. $S(q, \phi)$ is the structure factor, which contains information of interparticle interactions and spatial arrangement of particles. The incoherent background, I_b , is determined from the slope of a linear regression of the Porod plot (Iq^4 vs. q^4).¹³

For spherical particle suspensions, the total scattering intensity can be simplified as:

$$I(q) = \phi_p V_p (\Delta\rho_{SLD})^2 p(q) S(q) + I_b, \quad 2-26$$

where ϕ_p is the volume fraction of the particles in the suspension, V_p is the volume of single particle as $V_p = \frac{4\pi r^3}{3}$, $\Delta\rho_{SLD}$ is the SLD contrast (difference) between the particle and the suspension medium. The form factor $P(q)$ and structure factor $S(q)$ can be decoupled by using both dilute and concentrated particle suspensions. For dilute dispersions, the interactions between particles can be ignored and the structure factor $S(q) \sim 1$; hence information about the form factor can be extracted from the scattering intensity profile.

Static SANS measurements were performed at the National Institute of Standards and Technology (NIST) Center for Neutron Research (NCNR) in Gaithersburg, MD on both NG3 and NG7 beamlines. Samples were loaded into demountable titanium cells with a 1 mm path length. The temperatures of the samples were maintained at target temperature ± 0.1 °C using the 10 CB, 10 position sample

cell holder with fluid bath. A wide range of scattering wavevector q was obtained by combining scattering data from four different instrument configurations at detector distances of 1, 4, 13, and 15.3 m with lens. The wavelength for 1, 4, and 13 m configurations is 6.0 Å and 8.0 Å for 15.3 Å with lens. The SANS scattering intensity profiles were reduced to absolute scale and analyzed with the NIST data reduction and analysis macros in IGOR Pro available from NIST.¹⁴

2.6.1 Porod's Law

In the high- q domain, the scattering probes the internal configuration of the mass within the scattering objects. As $q \rightarrow \infty$, there is scattering contrast only at the interface between two media of different SLD. Porod derived the following relationship for the scattering intensity from the interfaces:¹³

$$I(q) \approx \frac{A}{q^4} + I_b, \quad 2-27$$

where A is the Porod constant, and I_b is the incoherent scattering cross-section, which is typically obtained by a “Porod plot” of Iq^n vs. q^n . $n = 4$ for objects with sharp interface, $n = 3-4$ for diffuse or rough interfaces.¹³

2.6.2 The Form Factor

In general, the form factor $P(q)$ is defined to describe the distribution of mass within a scattering object. It provides information about a single particle, such as shape, size, and polydispersity. Mathematically, form factor $P(q)$ can be obtained from the direct Fourier transform of the radial pair correlation function, $p(\vec{r}_{ij})$:^{13, 15}

$$P(q) = \int_{V_p} p(\vec{r}_{ij}) \exp(-iq \cdot \vec{r}_{ij}) d\vec{r}_{ij}, \quad 2-28$$

where the integral is taken over the volume of the scattering object. The pair correlation function $p(\vec{r}_{ij})$ describe the density probability of find a point of mass i within the object from a reference point j . In the literature, form factors have been derived for many prototypical and complex objects.¹⁵ For example, the model of monodispersed spherical objects for analyzing the structure of ionic liquid-water mixture and the model of polydispersed core-shell object for silica colloidal suspensions are discussed below.

Consider a monodisperse sphere of radius r and uniform density, the form factor is given by¹⁶

$$p(q) = \left(\Delta\rho_{SLD} \frac{3J_1(qr)}{qr} \right)^2, \quad 2-29$$

where the spherical Bessel function $J_1(x)$ is defined as:

$$J_1(x) = \frac{\sin x}{x^2} - \frac{\cos x}{x}. \quad 2-30$$

The expression for the form factor of a core-shell object with Schultz distributed core and constant shell is

$$\bar{P}(q, \rho_i, \phi, \bar{r}, p, \delta) = \int_0^\infty f(R, \bar{r}, p) \left[(\rho_{shell} - \rho_{solvent}) F(q, R + \delta) + (\rho_{core} - \rho_{shell}) F(q, R) \right]^2 dR \quad 2-31$$

in which the interference factor $F(q, R)$ for a spherical object in the Rayleigh–Gans–Debye limit is¹⁷

$$F(q, R) = 3V_p \frac{\sin(qR) - qR \cos(qR)}{(qR)^3}. \quad 2-32$$

The Schultz distribution function $f(R)$ is defined as

$$f(R) = (z+1)^{z+1} \left(\frac{R}{\bar{r}} \right)^2 \frac{\exp\left(- (z+1) \frac{R}{\bar{r}}\right)}{\bar{r} \Gamma(z+1)} \quad 2-33$$

$$z = \left(\frac{\bar{r}}{\sigma} \right)^2 - 1, \quad 2-34$$

where $\bar{r}$ is the average particle radius, σ is the standard deviation of radius, and $\Gamma(z+1)$ is the Gamma function.

In this dissertation, form factor model of monodispersed sphere is used to describe the properties of single micelle and water cluster in ionic liquid aqueous solutions. Schultz distributed spherical model and the associated core-shell models are fitted to the SANS data for dilute uncoated and coated silica particle dispersions.

2.6.3 The Structure Factor

The structure factor $S(q)$ generally is related to the arrangement and interactions between individual scattering objects. The structure factor $S(q, \bar{r})$ can be expressed as the Fourier transform of the pair distribution function,^{13, 15} $g(\vec{r})$, which is related to the potential of interaction between objects from statistical mechanics, and can be obtained using a liquid state theory such as the Ornstein–Zernike¹⁸⁻¹⁹ (OZ) equation:

$$S(q) = 1 + \bar{N} \int [g(\vec{r}) - 1] \exp(-iq \cdot \vec{r}) d\vec{r} \quad 2-35$$

$$g(\vec{r}) - 1 = c(\vec{r}) + \bar{N} \int c(|\vec{r} - \vec{r}_1|) (g(\vec{r}_1) - 1) d\vec{r}_1, \quad 2-36$$

where $\bar{N}$ is the number density of particles, $c(\vec{r})$ is the direct correlation function, which is related to the potential of mean force, $\Phi(r)$, between interacting particles.

Closer approximation: Percus–Yevick²⁰ approximation is used to calculate the direct

correlation function $c(\vec{r})$ for short-ranged interactions between particles, as shown below

$$c(r) = g(r) \left[1 - \exp \left(- \frac{\Phi(r)}{k_b T} \right) \right]. \quad 2-37$$

Sticky-hard sphere structure factor model is applied to evaluate the interaction between particles for a hard sphere fluid with a narrow attractive well. The strength of the attractive well is described in terms of "stickiness" parameter or the Baxter parameter is defined as

$$\tau_B = \frac{1}{12\varepsilon} \exp(\Phi_0 / k_B T) \quad 2-38$$

$$\varepsilon = \Delta / (a + \Delta), \quad 2-39$$

where Δ and a are separation distance.

The interaction potential between particles, $\Phi(r)$, as shown in Figure 2.7, is defined as²¹

$$\Phi(r) = \begin{cases} \infty & r < a \\ -\Phi_0 & a < r < a + \Delta \\ 0 & r > a + \Delta \end{cases} . \quad 2-40$$

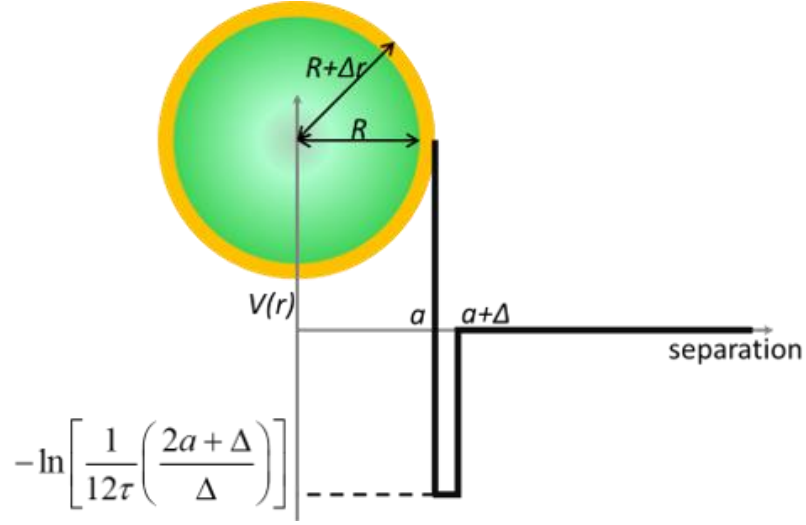


Figure 2.7: The graphical description of a sticky hard sphere potential for a coated particle system.

The perturbation parameter, ϵ , is between 0.01 and 0.1. The stickiness, τ_B , is representative of the attraction strength, and is related to the reduced second virial coefficient, B_2^* , by $\tau_B = \frac{1}{4(1 - B_2^*)}$. From the definition, it is clear that smaller τ_B means stronger attraction.

2.7 Small-Angle X-Ray Scattering (SAXS)

X-rays are electromagnetic waves and have shorter wavelength than light. It is able to probe the material structure on the length scale of 1-100 nm.²² SAXS method was used to characterize the microstructure of liquid solutions, complementary to SANS and other light scattering methods. SAXS shares the same experimental theory as for SANS with scattering intensity depending on the electron density contrast between structure and background using x-ray instead of neutron beam.¹³

SAXS measurements were conducted at the F2 BioSAXS beamline ($\lambda = 1.29$ Å) at the Cornell High Energy Synchrotron Source (CHESS) facility. The incident X-ray beam was aligned to a 250×250 exposure area. The path tubes were kept under vacuum to reduce scattering from air. The scattered signal was recorded by a Quantum 1CCD detector. Calibration was conducted using a silver behenate powder sample. Samples were pipetted manually into the funnel connected to the end of the capillary. BioXTAS RAW program²³ was used to reduce the 2D data to 1D data. The absolute intensity was obtained by normalizing to the incident beam intensity, and subtracting the background scattering of the solvent.

2.8 Quasi-Static Puncture Test

The puncture resistance of the Kevlar textile with or without shear thickening fluids treatment was evaluated by quasi-static puncture test. During the measurement, the ASTM F-1342 standard was followed. An A0 6-1/4" awl spike from Malco Products, Inc. was used to simulate the threat from round-edge objects and hypodermic needles of varying gauges were used to simulate the threat from sharp-edge objects. Between each experiment, the needle is replaced by a fresh one to ensure the same sharpness.²⁴ The spike or needle was held within the chunk that was mounted to a 500 N load cell on an Instron 5965. The single layer of Kevlar textile of 3 inch $\times$ 3 inch was mounted in a frame as shown in Figure 2.8, such that a circle of 6.35 diameter unbacked fabric was exposed. The spike or needle was loaded at a constant quasi-static speed approaching the textile. Zero displacement and zero force were defined when the probe nearly touched the fabric. The force experienced by the probe was recorded as a function of displacement. The maximum value of the force in the force-displacement curve was used to evaluate the force resistance of the tested

fabric. Twelve repeated experiments were conducted on each sample at different spots to obtain a good statistical value.

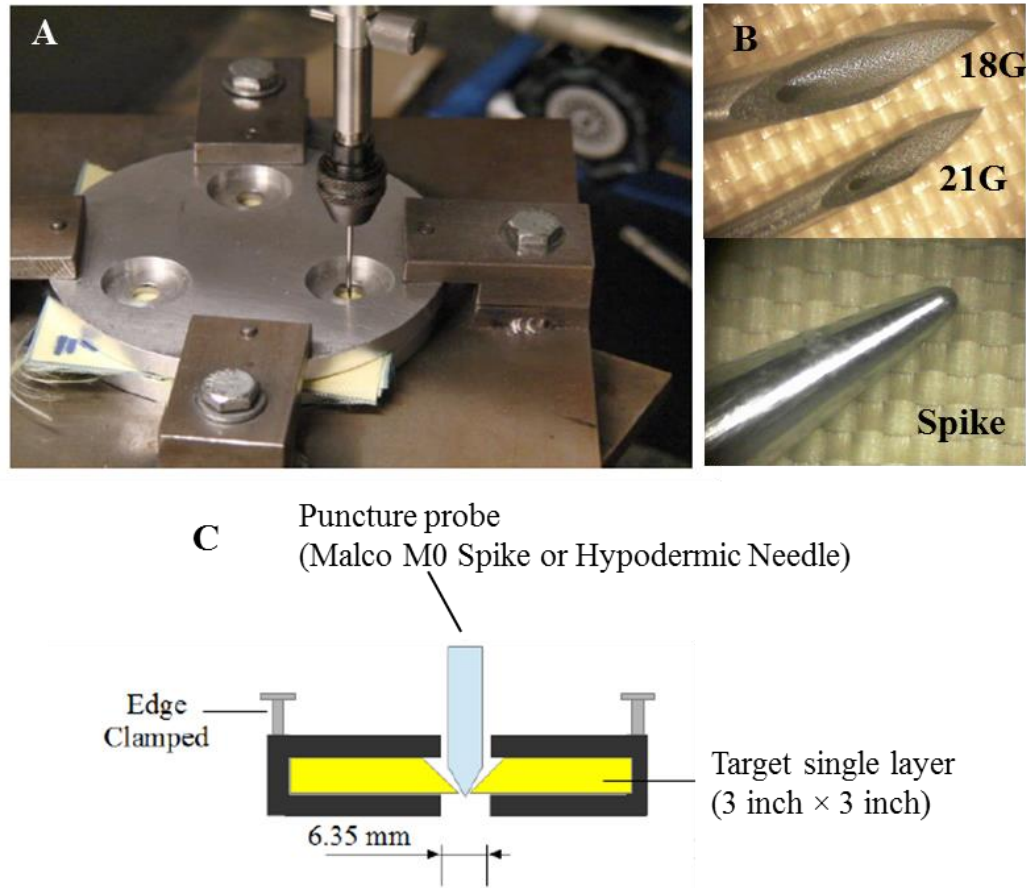


Figure 2.8: Set-up of quasi-static puncture test apparatus used to evaluate the quasi-static puncture resistance of Kevlar fabric with or without STFs treatment. (A) Photo of the modified ASTM F-1342 standard (with needle probe). (B) Optical image of hypodermic needles (18 G and 21 G) and Malco M0 spike on Kevlar 1148. (C) The dimensions of unbacked sample holder. Image courtesy of Dr. Colin D. Cwalina.

Because of the geometry of probe such as the spike and the needle, a typical force-displacement curve²⁵ initially shows gradual loading as the probe begins to push against the textile, with one or more dips in curves due to the partial tip breakthrough. In addition to that, yarns are deflected at a contact point at low displacements when using needle probe. After the force reaches the maximum value, a sharp force drop occurs as the probe tip penetrates through the textile completely. The point of puncture is defined as the point at which the force-displacement curve goes through a maximum value.²⁵ After the point of puncture, a long tail of low force is observed. For needle probe test, this low force is the result of sliding friction between the yarns and the barrel of the needle. For the spike probe test, however, there is a slightly increase in force after puncture point because the textile is pushed through and the diameter of the main shaft gradually increases.

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Chapter 3

EFFECT OF WATER ON PHYSICAL PROPERTIES AND STRUCTURES OF IONIC LIQUIDS

The purpose of this chapter is to describe the effect of addition of water molecules on the physical properties (density and viscosity) and microstructure of an ionic liquid $[\text{C}_4\text{mim}][\text{BF}_4]$. The phase transition of ionic liquid $[\text{C}_4\text{mim}][\text{BF}_4]$ -water mixtures covering the full composition range from high salt to low salt is investigated. At high salt levels, water molecularly dissolves into the network of ionic liquid $[\text{C}_4\text{mim}][\text{BF}_4]$ through hydrogen bond, and a water-ionic liquid hydrogen bond network is formed without formation of microphase. Densities and viscosities of the homogenous binary mixtures of $[\text{C}_4\text{mim}][\text{BF}_4]$ with water are reported for a temperature range of (283.15 to 373.15) K. A correlation between the excess mixture viscosity and the excess molar volume in the ionic liquid rich regime is identified, which is motivated by the free volume theory. As the water concentration increases (over the salt-rich regime), a microphase transition to water nanoclusters resembling an inverse microemulsion is identified and characterized using small angle neutron scattering (SANS). On the other hand, ionic liquid micelles form at low salt concentration due to the amphiphilic properties of cation $[\text{C}_4\text{mim}]^+$, as shown by small angle x-ray scattering (SAXS). A phase diagram for ionic liquid aqueous solutions (microphase separation, phase inversion, and micelle formation) is constructed, revealing similarities to traditional oil-water-surfactant systems. These results provide direct confirmation for recent simulations, as well insight into the source of non-

idealities in some thermophysical and transport properties (e.g., density and viscosity) of salt-rich aqueous mixtures reported in literature. Text and figures are reproduced and adapted with permission from Gao J., et al. *Langmuir* 2016, 32, (20), 5078–5084, and Gao J., et al. *Journal of Molecular Liquids* 2016, 223, 678-686.

3.1 Introduction

3.1.1 Densities and Viscosities of Ionic Liquid Aqueous Solutions

The physicochemical properties of ionic liquids and their mixture with organic/inorganic solvents are of importance for their industrial applications.¹⁻³ Therefore, thermodynamic properties such as density, viscosity, surface tension, refractive index, conductivity, and the speed of sound in binary mixtures of ionic liquids with molecular solvents are of great interest both from practical and theoretical point of view. Recently, systematic studies of the density, viscosity of ionic liquids [C_nmim][BF₄] with water,⁴⁻¹¹ alcohols,¹²⁻¹³ dimethyl sulfoxide (DMSO),¹⁴ ethylene glycol (EG)¹⁴ *et al.* over broad composition ranges have been reported. Of particular relevance for the work here, Rodriguez *et al.*¹⁵ studied the temperature and composition dependence of the density and viscosity of aqueous solutions of a series of 1-ethyl-3-methylimidazolium with varying anions, whereupon they suggested a trend between excess volume and viscosity.¹⁵ In this chapter, I have explored the thermodynamic relationships between transport and state properties in ionic liquid and water mixtures, and identified a new, semi-empirical relationship between non-idealities in viscosity and excess free volume that is motivated by free volume theory.

1-Butyl-3-methylimidazolium tetrafluoroborate, [C₄mim][BF₄], is among the most prevalently used and commonly investigated ionic liquids. Water contamination

is well known in ionic liquids,¹⁶ especially for ionic liquids, which have the tendency to mix with or dissolve in water, such as [C₄mim][BF₄]. The addition of trace amount of water into ionic liquids significantly changes the thermodynamic properties by affecting the microstructure.¹⁷⁻¹⁸ Therefore, in addition to the inherent importance of understanding the density and viscosity of binary mixture of [C₄mim][BF₄] with water, knowledge of excess properties provides insight into the molecular interactions in these mixtures and aids in developing structure-property relationships necessary for optimizing the properties of ionic liquids for specific applications.^{1, 19-20}

Herein, in section 3.3.2, I report the change of density and viscosity upon addition of water for [C₄mim][BF₄] in salt-rich regime (up to 40% water molar fraction) over the temperature range from 283.15 to 373.15 K and demonstrate a fundamentally new correlation between density and viscosity that aids in understanding the non-idealities in a wider range of ionic liquid aqueous mixtures. Neutron scattering measurements, which will be discussed in section 3.3.3.2, show solubility of water in the ionic liquid without microphase separation in this composition regime.²¹ The temperature dependence of density and dynamic viscosity of the aqueous mixtures are described by an empirical, linear relationship and by the Vogel-Fucher-Tammann (VFT) equation, respectively. Their excess properties are interpreted to evaluate the molecular interaction between the ionic liquid and water. The excess molar volumes are calculated using the measured experimental data and fitted to the Redlich-Kister equation. From this analysis, I discover a new correlation between the so-called “excess mixture viscosity”¹⁹ and the excess molar volume in the ionic liquid rich regime that is consistent with free volume theory. The non-ideal densities and viscosities are understood in terms of the interactions between cations

and anions of the ionic liquid and the water molecules. Finally, I explore the generality of this observation by analyzing published data on aqueous solutions of related ionic liquids.

3.1.2 Microstructure and Microphase Transition of [C₄mim][BF₄] Aqueous Solutions

As mentioned before, the density and viscosity of [C₄mim][BF₄] aqueous mixtures are non-ideal across the entire composition range. These non-idealities were attributed to specific water effects on the microstructure of the room temperature ionic liquids (RTIL),¹⁷ whereby water molecules hydrogen bond to the [BF₄]⁻ anions as reported by simulation²²⁻²³ and experiment.²⁴⁻²⁷

The molecular structure and interactions in mixtures of ionic liquids and water have been studied by both experimental techniques (e.g., NMR,²⁸ IR/Raman,²⁴⁻²⁵ fluorescence spectroscopy,²⁹ and SANS^{26, 30}) and molecular simulations.²² Due to their amphiphilicity, RTILs can self-assemble into micelle-like structures when diluted in solvents, similar to surfactants. This feature was evident in SANS measurements on dilute [C₄mim][BF₄], [C₈mim][I] and [C₈mim][Cl] aqueous solutions as reported by Bowers²⁶ and Almasy.³⁰ Surface tension and conductivity measurements for aqueous solutions of [C₄mim][BF₄] also display distinct break points characteristic of aggregation of the ionic liquid salts.²⁶ Singh *et al.* employed NMR and conducted a detailed analysis of chemical shifts of water and various protons of ionic liquids ([C₄mim][BF₄], [C₄mim][Cl], [C₈mim][Cl], N-butyl-3-methylpyridinium chloride ([C₄mpy][Cl])) aqueous solutions to probe the aggregation structure.^{28, 31} The conformational changes in a variety of RTILs induced by the self-aggregated of ionic liquid are shown to depend on the aromatic ring, alkyl chain,

counter ions, and their interactions with water.²⁸ In Section 3.3.3.1, I study the formation and growth of micellar structure of [C₄mim][BF₄] in water solutions with various concentrations at room temperature through SAXS. The shape and size of micellar structure are evaluated and compared quantitatively using monodispersed sphere and ellipsoid form factor model fittings. The growth of micelle is illustrated to be along one direction forming “rod” like shape micelle.

The opposite end of the composition spectrum, rich in RTIL, is equally interesting, but perhaps less understood.^{22, 24-25} Research shows that the interaction between the anion and water generally dominates for salt-rich region of [C₄mim][BF₄]-water mixtures, with individual water molecules forming hydrogen bonds with two [BF₄]⁻ anions without substantially disrupting the nanoscale structuring present in the ionic liquid.^{22, 17, 18, 19, 20} However, with increasing water addition, water molecules begin to associate, forming dimers and eventually larger clusters. Furthermore, the ionic liquid’s nanostructure, which is regulated by strong electrostatic interactions between the cations and anions, is gradually disrupted with increasing water addition.²² Further addition of water leads to a sequence of micro-phase transitions from ionic liquid polar networks to water clusters in the RTIL, which self-aggregates in water, and finally to dilute ionic liquid electrolytes in water. These phase transitions and properties are revealed by molecular simulation²² and experiments.²⁴⁻²⁷

Water and methanol associations in ionic liquids have been studied by FTIR spectroscopy.²⁴ At low water content, spectral features in the OH stretching region reveals that most of the water and methanol molecules tend to be isolated from each other and interact with the anion of the IL through hydrogen bonding. Self-association

of water (and methanol) molecules is evident in $[\text{C}_2\text{mim}][\text{BF}_4]$ and $[\text{C}_4\text{mim}][\text{BF}_4]$ at higher water (methanol) concentrations. Shirota *et al.*²⁵ investigated the state of molecular association in $[\text{C}_n\text{mim}][\text{BF}_4]\text{-H}_2\text{O}$ and $[\text{C}_n\text{mim}][\text{NTf}_2]\text{-H}_2\text{O}$ mixtures by Raman and IR spectroscopy and reported that water structure is similar for mixture with RTILs with varying cation alkyl length. This result confirms that water aggregation in RTILs is mainly determined by association of the water with ionic groups in the RTILs and less by the hydrophobicity of the cations.

As discussed, the presence of water clusters in salt-rich RTIL aqueous mixtures has been proposed in experiments²⁴⁻²⁷ and predicted by simulations;²²⁻²³ however, the nanoscale structure of such water clusters has not been measured directly. In section 3.3.3.2, I investigate the effects of addition of deuterated water on the nanoscale structure of $[\text{C}_4\text{mim}][\text{BF}_4]$ at room temperature. SANS measurements quantitatively determine the microstructure in the salt-rich mixtures with varying water content. Distinct water structures are revealed in these aqueous solutions with increasing water content, indicating that water clusters in the form of an inverse microemulsion form from the excess water once the ions are fully hydrated, confirming prior hypotheses and simulations.

3.2 Materials and Methods

3.2.1 Materials

The RTIL $[\text{C}_4\text{mim}][\text{BF}_4]$ (>99% pure, 226 g/mol, from Iolitec, batch# K00119.1.Inc, The reported purities from manufacture are: cation 99.8%, anion 99.9%, halides <100 ppm, water 151 ppm.), was dehydrated under vacuum condition at 70 °C for 24 h prior to use. The water content was measured in our lab and determined to be

373 ppm by Karl Fischer titration. Millipore deionized water with resistivity of 18.2 M Ω ·cm (25 °C) was used to prepare aqueous ionic liquid solutions for density and viscosity measurements. Deuterated water (D₂O, 99.8% pure, Cambridge Isotope Lab. Inc) was used for enhancing contrast in SANS measurement. Both the ionic liquid and water were filtered using 200 nm nylon membrane syringe filter before mixing. The samples were prepared gravimetrically and the results reported on both weight and molar fraction basis. The uncertainty in the samples' mass fraction is within 3% of mass fraction for each sample. The mass fractions of water in samples and the corresponding molar fractions are listed in Table 3.1. All samples were prepared freshly right before measurements. Density and viscosity measurements were completed within 30 min. Samples were sealed in glass tube which prevented the water absorption during measurements. SANS measurement for each sample was finished within 10 min and samples were loaded to SANS titanium cell sealed with o-ring to prevent any possible humidity effects in samples during measurement. The effect of hydrolysis of [C₄mim][BF₄] in aqueous solution on our SANS, density and viscosity measurements was proved to be negligible based on the ¹⁹F NMR measurements in Figure 3.1.

Table 3.1: [C₄mim][BF₄]-water mixtures compositions in mass fraction and molar fraction.

Density & viscosity measurements		
Sample #	H ₂ O mass fraction in mixture*	H ₂ O molar fraction in mixture
1	0.28 wt%	0.03
2	0.52 wt%	0.06
3	1.01 wt%	0.11
4	2.03 wt%	0.21
5	3.01 wt%	0.28
6	5.00 wt%	0.40
SANS measurements		
Sample #	D ₂ O mass fraction in mixture*	D ₂ O molar fraction in mixture
1	3.02 wt%	0.26
2	4.97 wt%	0.37
3	11.01 wt%	0.58
4	14.97 wt%	0.67
5	20.00 wt%	0.74
6	22.01 wt%	0.76
7	25.03 wt%	0.79
8	26.98 wt%	0.81
9	30.02 wt%	0.83

* The uncertainty of samples' mass fraction is within 3% of mass fraction for each sample.

3.2.2 Fluorine Nuclear Magnetic Resonance Spectroscopy (¹⁹F NMR)

¹⁹F NMR spectra were measured on Bruker AV400. Ionic liquid [C₄mim][BF₄] and its aqueous solution were dissolved in deuterated chloroform (CDCl₃) before measurement. MestReNova NMR software was used to perform spectra analysis.

3.2.3 Density Measurements

The densities of pure ionic liquid [C₄mim][BF₄] and of its aqueous mixtures at atmospheric pressure were measured with an oscillating U-tube densitometer Anton Paar DMA 4500 M at temperatures from 283.15 K to 363.15 K with Peltier temperature control with an accuracy of ± 0.03 K. The densitometer was calibrated with dry air and ultra-pure water at atmospheric pressure.

3.2.4 Viscosity Measurements

Kinematic viscosities were measured using an Anton Paar AMVn automated microviscometer at temperatures from 293.15 K to 373.15 K at atmospheric pressure condition. The temperature was controlled by a built-in Peltier within 0.05 K. Measurements were made with three different angles using calibrated capillary of $d = 3.0$ mm and stainless steel balls of $d = 2.5$ mm following standard protocols³² and repeated four times for each angle. The viscosities and standard deviations were reported as the uncertainty in Appendix A (Table A.1) for each composition and temperature. The instrument's accuracy for measuring time is reported to be 0.002 s. The reproducibility of the instrument used for viscosity measurement was within 0.35% and the reproducibility between samples was within 0.7%. Dynamic viscosities are reported here, which are the product of the measured kinematic viscosities and the density.

3.2.5 Small-Angle Neutron Scattering (SANS)

SANS measurements were performed at the National Institute of Standards and Technology (NIST) Center for Neutron Research (NCNR) in Gaithersburg, MD on both NGB 30 and NG7 beamlines. Samples were loaded into demountable titanium cells with a 1 mm path length. The cell temperatures were maintained to ± 0.1 °C

using the 10 CB, 10 position sample cell holder with fluid bath. A high scattering wavevector q range was achieved by obtaining scattering intensity from one instrument configuration at detector distances of 1 m. The wavelength for 1 m configurations is 6.0 Å. The SANS scattering intensity profiles were reduced to absolute scale and analyzed with the NIST data reduction and analysis macros in IGOR Pro available from NIST.³³

3.2.6 SANS Data Analysis

The properties of the ionic liquid aqueous solution with water clusters were determined by modeling the measured SANS intensity with a monodisperse sphere form factor using software packages provided the Center for Neutron Research.³³ The scattering length density (SLD) of water and pure ionic liquid [C₄mim][BF₄] were calculated using the measured water density (Table 3.2) at 25 °C by NIST NCNR online tool: Neutron activation and scattering calculator. I assumed that the deuterated water clusters could be modeled as monodisperse spheres with the properties of pure D₂O. The volume fraction of water clusters determined from the fitting was used to calculate the volume fraction and molar fraction of deuterated water molecularly dissolved in the ionic liquid. For simplicity, ideal mixing was assumed to calculate the water distributions in dissolved state and microphase separated state. The SLD of ionic liquid-water mixture in dissolved state were calculated using the additive equation:

$$SLD_m = \phi_{IL} SLD_{IL} + \phi_w SLD_w \quad 3-1$$

where ϕ_{IL} and ϕ_w are the volume fraction of ionic liquid [C₄mim][BF₄] and deuterated water in dissolved state, respectively; SLD_{IL} and SLD_w are the SLD of pure ionic

liquid [C₄mim][BF₄] and deuterated water at 25 °C, respectively (Table 3.2). This calculated SLD of ionic liquid-water mixture in dissolved state was compared with the SLD of the same phase from SANS fitting to evaluate the validation of SANS fitting results.

Table 3.2: Density, molecular mass, and SLD of ionic liquid [C₄mim][BF₄] and D₂O at 25 °C.

Materials	ρ (g/cm ³ , 25 °C)	M_w (g/mol)	SLD (Å ⁻²)
[C ₄ mim][BF ₄]	1.201	226	1.40×10^{-6}
D ₂ O	1.107	20	6.38×10^{-6}

3.3 Results and Discussion

3.3.1 Hydrolysis Analysis of Ionic Liquid [C₄mim][BF₄] with Present of Water

Aqueous solutions of tetrafluoroborate ([BF₄]⁻) and hexafluorophosphate ([PF₆]⁻) based ionic liquids are reported to hydrolyze, liberating side products such as [BF₃OH]⁻ and hydrogen fluoride.³⁴⁻³⁵ However, the degradation rate depends on water content, temperature, pH, and time since preparation. Freire *et al.*³⁵ reported that [C₄mim][BF₄] aqueous solutions with particularly high water content (~ 50 wt%, 93 mol%) decompose to ~2% side products after heated to 373 K for 30 min.

The density or viscosity measurements herein were conducted at temperature range from 283.15 K to 373.15K and the tests were completed within 30 min. Considering the low water contents (≤5 wt%) and low temperature range, the decomposition rate is likely lower than 2%. Our ionic liquid-D₂O aqueous solution samples were prepared freshly right before SANS measurement and loaded to SANS

titanium cell sealed with o-ring to prevent possible humidity effects in samples during measurement. Our SANS measurement on each sample were able to be completed within 10 min at 298 K, and measurements on all samples were finished in 80 min. Based on the low water contents, low temperature, and short time, the decomposition rate would be even lower than 2%. I performed ^{19}F -NMR measurements for pure $[\text{C}_4\text{mim}][\text{BF}_4]$, $[\text{C}_4\text{mim}][\text{BF}_4]$ aqueous solution with 5 w% H_2O after 30 min at 298.15 K, and $[\text{C}_4\text{mim}][\text{BF}_4]$ aqueous solution with 5 w% H_2O measured after density and viscosity measurements for the entire temperature range in deuterated chloroform (CDCl_3) and shown in Figure 3.1. The ^{19}F -NMR spectra of the pure IL show no other peaks besides the one at -151.6 ppm, which corresponds to the anion $[\text{BF}_4]^-$. In addition to this peak, for the $[\text{C}_4\text{mim}][\text{BF}_4]$ aqueous solution with 5 w% H_2O at 298.15 K and for the one taken after density and viscosity measurements, these two aqueous samples show a small peak at -150.7 ppm, which indicates the decomposition of the anion $[\text{BF}_4]^-$. However, as seen, the decomposition peak intensities are very low, such that the decomposition rate is negligible, when compared with the un-hydrolyzed $[\text{BF}_4]^-$ anion. The effect of $[\text{C}_4\text{mim}][\text{BF}_4]$ hydrolysis on density/viscosity/SANS measurement results can be neglected.

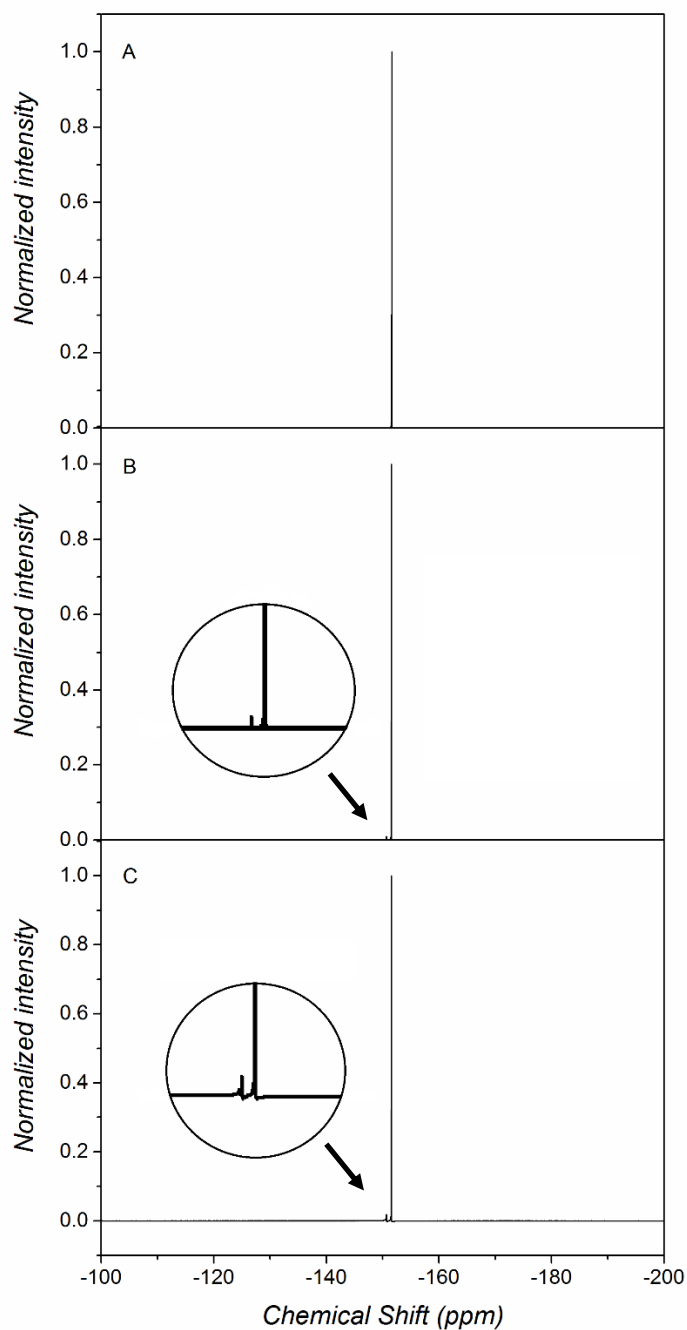


Figure 3.1: ^{19}F -NMR spectrum of pure $[\text{C}_4\text{mim}][\text{BF}_4]$ (A), $[\text{C}_4\text{mim}][\text{BF}_4]$ aqueous solution with 5 w% H_2O after 30 min at 298.15 K (B) and $[\text{C}_4\text{mim}][\text{BF}_4]$ aqueous solution with 5 w% H_2O after density/viscosity measurement for the entire temperature range (C) in CDCl_3 .

3.3.2 Physical Properties Dependence

Density and viscosity measurements for the pure ionic liquid $[\text{C}_4\text{mim}][\text{BF}_4]$ over the temperature range 283.15 K to 373.15 K are compared with the available literature data in Figure 3.2. The corresponding comparisons for $[\text{C}_4\text{mim}][\text{BF}_4]$ - water systems with various water contents at 298.15 K are shown in Figure 3.3. A satisfactory agreement is found. The densities and viscosities results show minor differences (with a few outlier points in the literature data), which may be attributable to differences in sample purity, i.e., the accuracy of the reported data is generally limited by the sample purity.

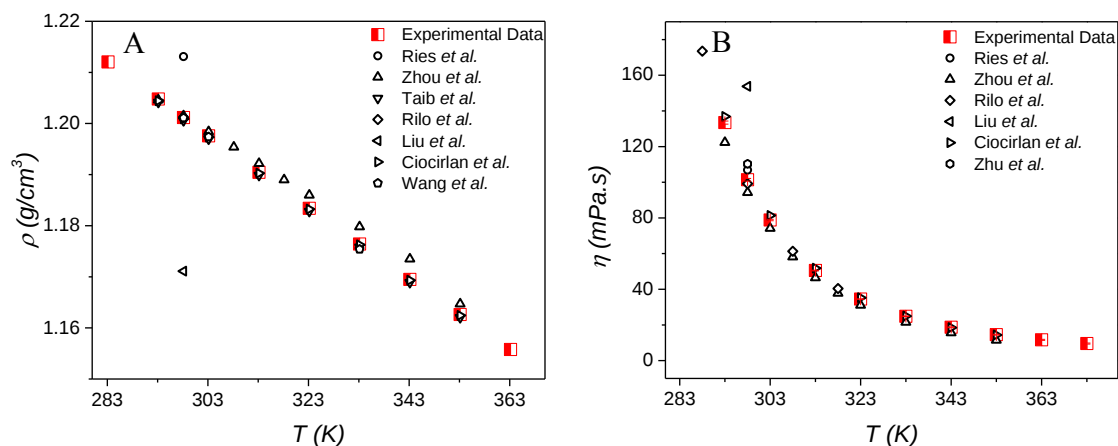


Figure 3.2: Comparison of measured densities and dynamic viscosities with literature values for pure $[\text{C}_4\text{mim}][\text{BF}_4]$ at temperatures from 283.15 K to 373.15 K. The literature data are from: Ries *et al.*,⁴ Zhou *et al.*,⁵ Taib *et al.*,⁶ Rilo *et al.*,^{7,36} Liu *et al.*,⁹ Ciocirlan *et al.*,¹⁴ Wang *et al.*,³⁷ and Zhu *et al.*³⁸

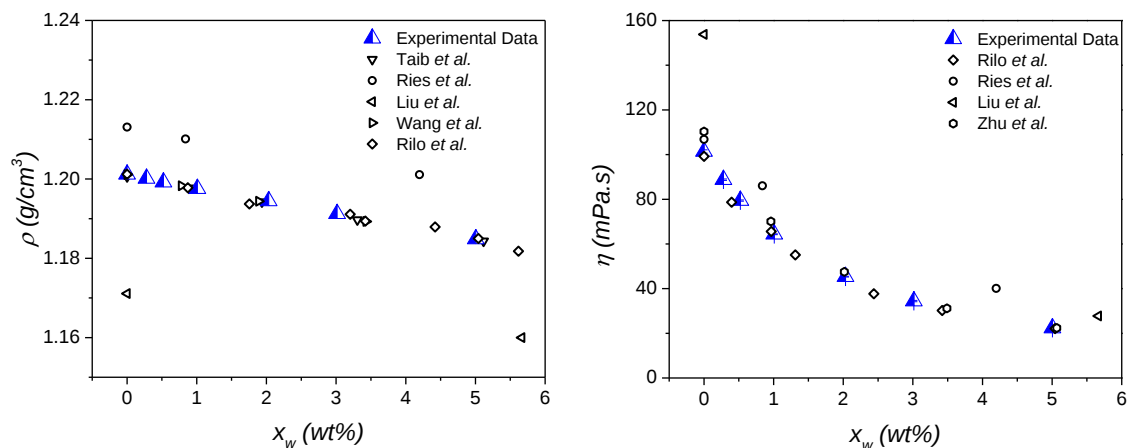


Figure 3.3: Comparison of measured densities and dynamic viscosities with literature values at 298.15 K for $[\text{C}_4\text{mim}][\text{BF}_4]$ with various water contents. The literature data are from: Ries *et al.*,⁴ Taib *et al.*,⁶ Rilo *et al.*,^{7,36} Liu *et al.*,⁹ Wang *et al.*,³⁷ and Zhu *et al.*³⁸

3.3.2.1 Density

The densities of $[\text{C}_4\text{mim}][\text{BF}_4]$ aqueous solutions with respect to water weight fraction and temperature are shown in Figure 3.4 and in Table A.1 (see Appendix A). The addition of small amounts of water decreases the mixture density, which also decreases with temperature. Figure 3.4A shows that the density decreases linearly with the water mass fraction at each temperature, and the values of the linear fits are given in Table 3.3. The density decreases with increasing temperature, as shown in Figure 3.4B, but the relative effect of water addition is nearly insensitive to temperature. A linear correlation between density and temperature is observed for each composition as shown in Figure 3.4B and the fitting parameters are also given in Table 3.3. These linear correlations between density and water weight fraction and/or temperature are also useful for determining water content from density experiments.

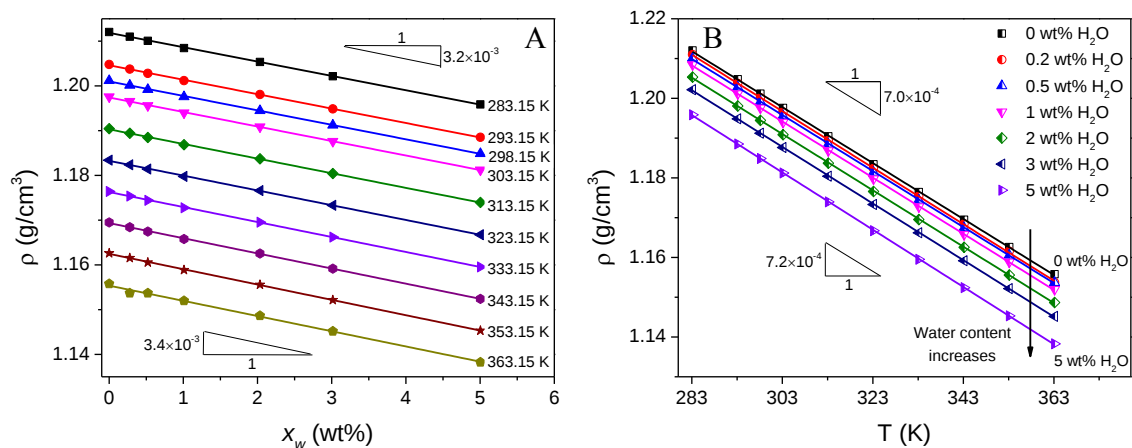


Figure 3.4: The densities of [C₄mim][BF₄] aqueous solution for varying water content (A) and temperature (B). Solid lines represent the linear correlations, respectively.

Table 3.3: Fitting parameters of the linear relation of density - water content (Figure 3.4A) and density - temperature (Figure 3.4B) for ionic liquid aqueous solutions.

Density-Water content (Figure 3.4A)					
T(K)	Slope	Intercept (g/cm ³)	T(K)	Slope	Intercept (g/cm ³)
283.15	3.21×10^{-3}	1.212	323.15	3.30×10^{-3}	1.183
293.15	3.22×10^{-3}	1.205	333.15	3.35×10^{-3}	1.176
298.15	3.23×10^{-3}	1.201	343.15	3.39×10^{-3}	1.169
303.15	3.24×10^{-3}	1.197	353.15	3.43×10^{-3}	1.162
313.15	3.27×10^{-3}	1.190	363.15	3.40×10^{-3}	1.155
Density-Temperature (Figure 3.4B)					
x_w (wt%)	Slope	Intercept (g/cm ³)	x_w (wt%)	Slope	Intercept (g/cm ³)
0.00	-7.03×10^{-4}	1.412	2.03	-7.08×10^{-4}	1.406
0.28	-7.10×10^{-4}	1.411	3.01	-7.12×10^{-4}	1.403
0.52	-7.04×10^{-4}	1.409	5.00	-7.20×10^{-4}	1.400
1.01	-7.06×10^{-4}	1.408			

The experimental densities for the binary mixtures are compared with calculated densities based on ideal mixing theory in Figure 3.5, where negative deviations from ideal mixing are observed for all mixtures. The negative deviations indicate an expansion of the ionic liquid microstructure with the addition of small amounts of water. The excess molar volumes $\underline{V}^{ex}$ are calculated as:

$$\underline{V}^{ex} = \frac{x_{IL}M_{IL} + x_wM_w}{\rho_m} - \frac{x_{IL}M_{IL}}{\rho_{IL}} - \frac{x_wM_w}{\rho_w} \quad 3-2$$

where ρ_m is the density of the mixture; x_{IL} and x_w are the molar fraction of ionic liquid and water, respectively; M_{IL} and M_w are the molecular weight of pure ionic liquid and water. The values of $\underline{V}^{ex}$ shown in Figure 3.6A at several temperatures are fitted to the Redlich-Kister polynomial equation:

$$\underline{V}^{ex} = x_w x_{IL} \sum_{i=0}^m A_i (x_w - x_{IL})^i \quad 3-3$$

Where A_i are the fitting coefficients, m is the order of the Redlich-Kister polynomial equation, x_w and x_{IL} are the molar fraction of water and ionic liquid in the aqueous mixtures. Good fits are achieved with $m = 3$ and the fitting parameters are reported in Table A.2 (See Appendix A). The excess molar volume of $[C_4mim][BF_4]$ aqueous solutions with water content in the range 0-5 wt% (0-0.4 molar fraction) can be predicted using these parameters. Figure 3.6A shows that the values of excess molar volume are positive at all temperatures and over the solution compositions studied. The values of $\underline{V}^{ex}$ are expected to eventually decrease for compositions $x_w > 0.4$ as reported for other ionic liquids mixture systems.^{4, 6, 12}

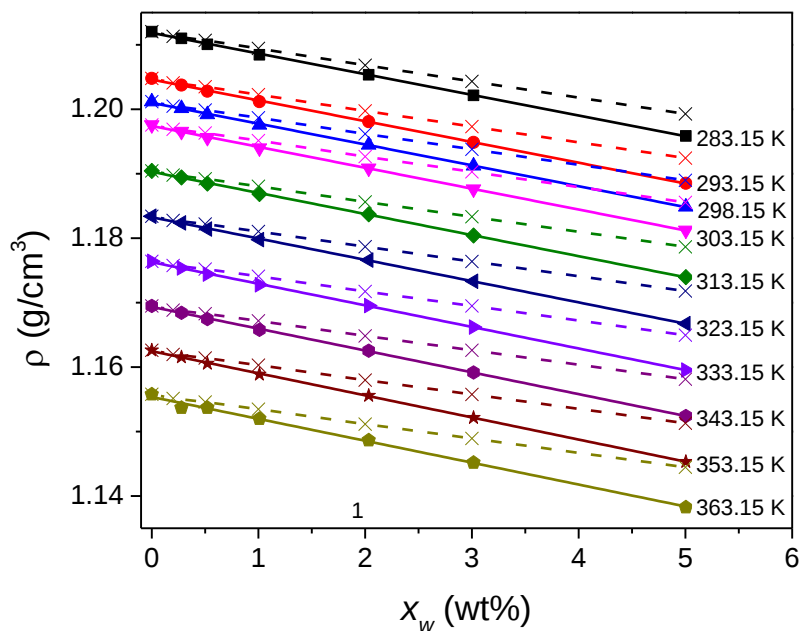


Figure 3.5: The experimental densities of $[C_4mim][BF_4]$ aqueous solution at different water contents compared with calculated densities based on ideal mixing theory. The solid/dash lines represent the linear correlations between experimental/calculated density and water mass fraction.

The measurement of positive excess molar volumes is consistent with the reported structure of isolated water molecules hydrogen bonding to two anions via hydrogen bonds for trace water in ionic liquid as reported by simulation²² and experiments.²⁴ The intercalation of water into the ionic bonds in the ionic liquid is expected to expand the ionic liquid. Further evidence for this can be found in the work of Ries *et al.*,⁴ whose study of the conductivity and infrared spectra (IR) of $[C_4mim][BF_4]$ water solutions at room temperature shows that the solution conductivities increase due to the weakening of the intermolecular interaction between the anionic and cationic species of $[C_4mim][BF_4]$ upon the addition of water. The

magnitude of $\underline{V}^{ex}$ increases with increasing temperature, as shown in Figure 3.6B. This increase is expected due to the further weakening of the ionic interactions at increasing temperatures. Our data show that the $\underline{V}^{ex}$ of mixture solutions with higher water concentrations are more strongly affected by temperature.

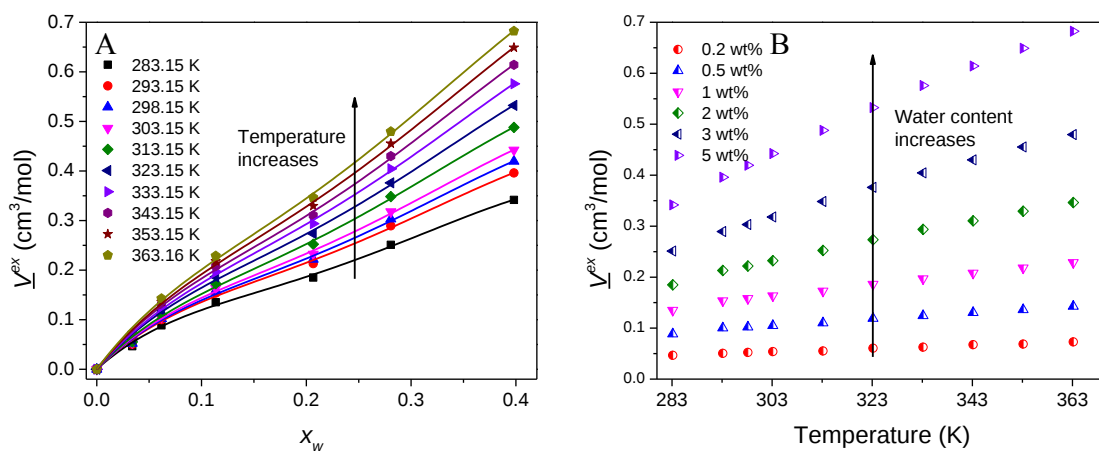


Figure 3.6: Excess molar volume $\underline{V}^{ex}$ of [C₄mim][BF₄] aqueous solution dependence on water molar fraction x_w (A) and temperature (B). The symbols represent experimental value. The solid lines are fits to the Redlich-Kister equation.

3.3.2.2 Viscosity

The viscosities of the ionic liquid aqueous mixtures are observed to decrease strongly with the addition of water and increase in temperature as shown in Figure 3.7A. Importantly, the viscosity decreases significantly with the addition of small amount of water. The viscosity dependence on water molar fraction shown in Figure 3.7A can be correlated by an exponential function:

$$\eta = \eta_0 \exp(-x_w / a) \quad 3-4$$

where η is the viscosity of the aqueous solution at certain temperature, η_0 is the viscosity of pure ionic liquid at the same temperature, x_w is the molar fraction of water and a is a fitting constant reported in Table A.3 (See Appendix A). The sensitivity to water addition increases with temperature, as evident by the values of the fitting constant a , which increases from 0.24 at 293.15 K to 0.54 at 373.15 K.

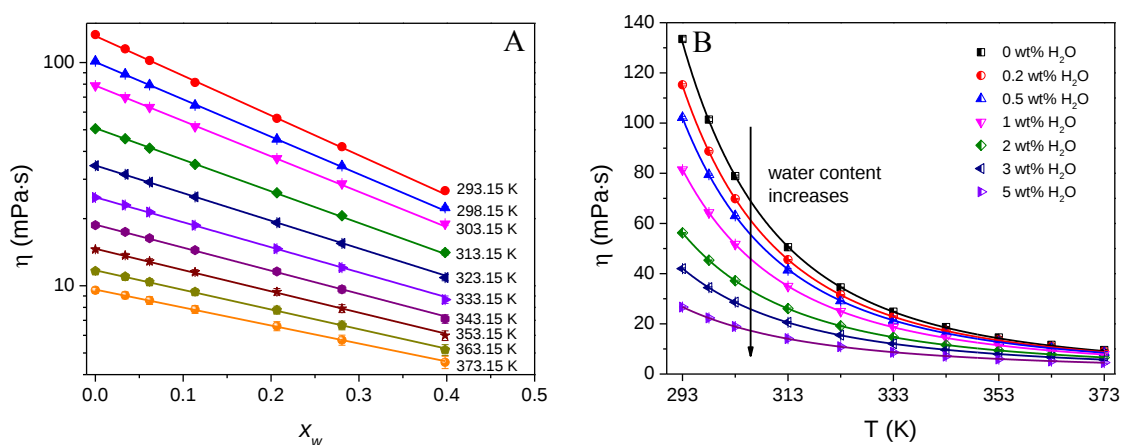


Figure 3.7: The viscosities of $[\text{C}_4\text{mim}][\text{BF}_4]$ aqueous solution at different water molar fraction (A) and temperatures (B). Solid lines represent an empirical correlation (A) and the Vogel-Fulcher-Tammann (VFT) equation correlation (B), respectively.

The mixture viscosities decrease with temperature as shown in Figure 3.7B. This behavior can be accurately described by the Vogel-Fulcher-Tammann (VFT) equation:

$$\eta = AT^{1/2} \exp[B/(T - T_0)] \quad 3-5$$

where A , B and T_0 are the fitting parameters. T_0 is the ideal transition temperature, which is often associated with but lower than the glass transition temperature,¹⁴ and the glass transition temperature is reported to be 193.6 K for the pure ionic liquid [C₄mim][BF₄] as determined using differential scanning calorimetry.³⁹ Domanska *et al.*⁴⁰ and Ferry⁴¹ proposed using the ideal transition temperature for T_0 , for glass-forming ionic liquids and their mixtures with organic solvents. Ciocirlan *et al.*¹⁴ set the value of T_0 to be 170 K for the [C₄mim][BF₄]/ dimethyl sulfoxide (DMSO) and [C₄mim][BF₄]/ ethylene glycol (EG) mixtures to correlate the temperature dependence of the viscosity. For the ionic liquid aqueous solution system studied here, the ideal transition temperature T_0 is set as one fitting parameter and determined empirically with other two parameters A and B for the aqueous [C₄mim][BF₄] mixtures investigated. Equation 3-5 provides a successful correlation of the viscosity measurements, as shown in Figure 3.7B. The fitting parameters A , B and T_0 are listed in Table 3.4. The ideal transition temperature T_0 decreases with the addition of water as shown in Table 3.4. The obtained ideal transition temperatures T_0 at various water contents are consistent (slightly smaller) with corresponding glass transition temperatures of [C₄mim][BF₄]-water solutions measured by differential thermal analysis (DTA).⁴² Moreover, Yoshimura⁴² found the measured glass transition temperature of [C₄mim][BF₄]-water solutions decreases with water content in the salt-rich regime until microphase separation. In the water-rich regime, the formation of water clusters has led to an increased glass transition temperature. Previous study using neutron scattering measurements have illustrated that the composition regime studied herein have no microphase separation.²¹ Thus, the ideal transition temperatures obtained from the VFT fitting are in agreement with the glass transition

temperature measured by DTA in the same salt-rich regime. I note that the VFT equation provides a better correlation of the viscosity data than a simple Arrhenius plot (see Appendix A - Figure A.2), which was suggested by Haghani *et al.*, who modeled an extensive variety of binary ionic liquid mixtures.⁴³

Table 3.4: Fitting parameters (A , B and T_0) of the VFT equation for $[\text{C}_4\text{mim}][\text{BF}_4]$ aqueous solutions with various compositions.

Water content	A	B	T_0
<i>wt %</i>	<i>mPa.s.K^{-0.5}</i>	<i>K</i>	<i>K</i>
0	0.0106	734.0	181.8
0.28	0.0097	760.4	176.8
0.52	0.0089	780.1	173.1
1.01	0.0095	757.0	171.3
2.03	0.0102	716.1	169.0
3.01	0.0099	707.0	164.9
5.00	0.0096	675.7	160.4

Although there is no established theory for the viscosity of ideal binary mixtures, there have been many models proposed and experimental studies directed towards validating these models (see⁴⁴⁻⁴⁵ for example). The viscosity of ideal mixtures can be calculated according to the Arrhenius ideal solution model,⁴⁶⁻⁴⁸ which is equivalent to the fluidity additivity rule:

$$\log(\eta_{ideal}) = x_{IL} \log(\eta_{IL}) + x_w \log(\eta_w) \quad 3-6$$

where η_{ideal} , η_{IL} and η_w are the viscosities of the ideal mixture, pure ionic liquid and water, respectively. To quantify the viscosity deviation from ideal behavior for the ionic liquid 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide

([Hmim][Tf₂N]) and 1-octene mixtures, Ahosseini and Scurto¹⁹ introduced the “excess viscosity” as the difference between the mixture viscosity and the ideal viscosity. I adopt this nomenclature convention in our study of the [C₄mim][BF₄] and water mixtures. Here, the excess log viscosity $(\log \eta)^{ex}$ is defined as the difference between the logarithm of the mixture viscosity and ideal mixture viscosity defined by Arrhenius:⁴⁶⁻⁴⁸

$$(\log \eta)^{ex} = \log(\eta) - \log(\eta_{ideal}) \quad 3-7$$

The ideal mixture viscosities calculated from Equation 3-6 are compared with experimental results in Figure 3.8A and the excess viscosities are plotted vs water molar fraction in Figure 3.8B. Positive deviations from ideal mixing are an indication of strong interactions between the water and the [C₄mim][BF₄], such that water does not exhibit its bulk viscosity as anticipated in the Arrhenius ideal mixing theory.

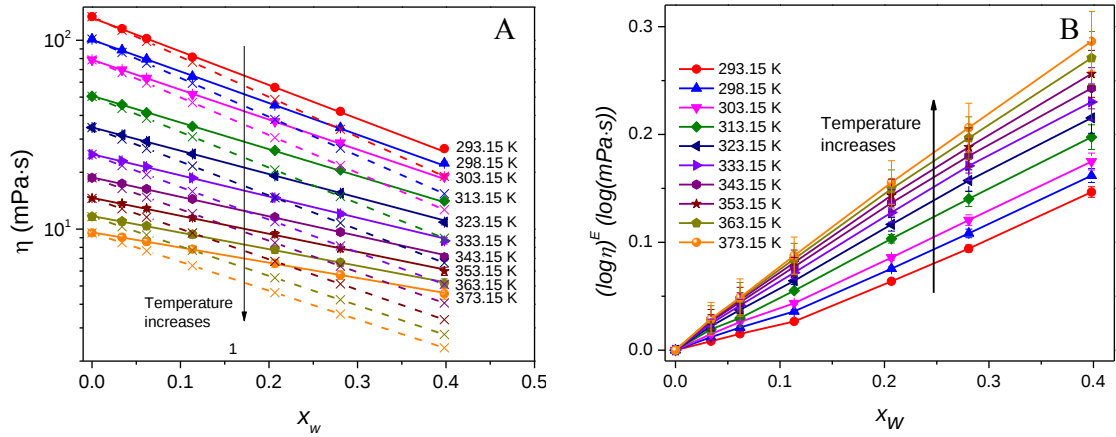


Figure 3.8: (A) Viscosities of $[C_4mim][BF_4]$ aqueous solutions as a function of water mole fraction (solid lines and symbols) compared with calculated viscosities based on ideal mixing theory (-x-). (B) Excess log viscosity, $(\log \eta)^{ex}$, vs molar fraction of water x_w for $[C_4mim][BF_4]$ aqueous mixtures as a function of temperature.

3.3.2.3 Density-Viscosity Correlation

Doolittle *et al.*⁴⁹ related the dynamic viscosity of simple liquids with the free volume in solution $\underline{V}_f$, with an empirical equation that has successfully modeled the viscosity of ordinary liquids:

$$\log \eta = \log A + B \frac{\underline{V} - \underline{V}_f}{\underline{V}_f} \quad 3-8$$

where A and B are empirical constants, $\underline{V}$ and $\underline{V}_f$ are the molar volume and molar free volume of the liquid. Based on the Doolittle equation, I propose the following, semi-empirical relationship between the excess viscosity and the excess volume:

$$(\log \eta)^{ex} = C \underline{V}^{ex} \quad 3-9$$

where C is an empirical constant, which is taken to be independent of temperature and composition.

The physical basis for this semi-empirical relationship lies in the expectation that the excess molar volume arises from the strong interaction between the water and the ionic liquid at lower water content. Thus, the positive excess molar volume reflects the binding of water into the ionic domains of the IL. Hence, the viscosity of the water in this bound state is significantly greater as compared to water in the free-state. According to the Doolittle application of free volume theory, this excess molar volume acts to increase the viscosity above what would be expected for ideal mixing. Note that a possible relationship between the excess mixing properties, including the viscosity and molar volume, and free volume theory has been explored for binary liquid mixtures for over forty years,⁴⁸ but a formal relationship of the form of Equation 3-9 has not been derived or validated. Therefore, I propose it as a semi-empirical relationship to be tested against experimental data.

For the [C₄mim][BF₄] aqueous solutions, it is found that excess log viscosity $(\log \eta)^{ex}$ is indeed linearly correlated with the excess molar volume $\underline{V}^{ex}$ ($R^2 = 0.996$) over the range of compositions and temperatures studied as shown in Figure 3.9. This new correlation provides insight into the significant effect of water on the viscosity of ionic liquids. The relative residues of the excess log viscosity $(\log \eta)^{ex}$ from the correlation fitting for different temperatures and various water compositions are shown in Figure 3.10. The relative residues in Figure 3.10 indicate that significant deviations occur at low water content and at lower temperature, with the maximum relative deviation at water molar fraction $x_w = 0.06$ composition with temperature 293.15 K. Correlation improves with increasing water content and temperature.

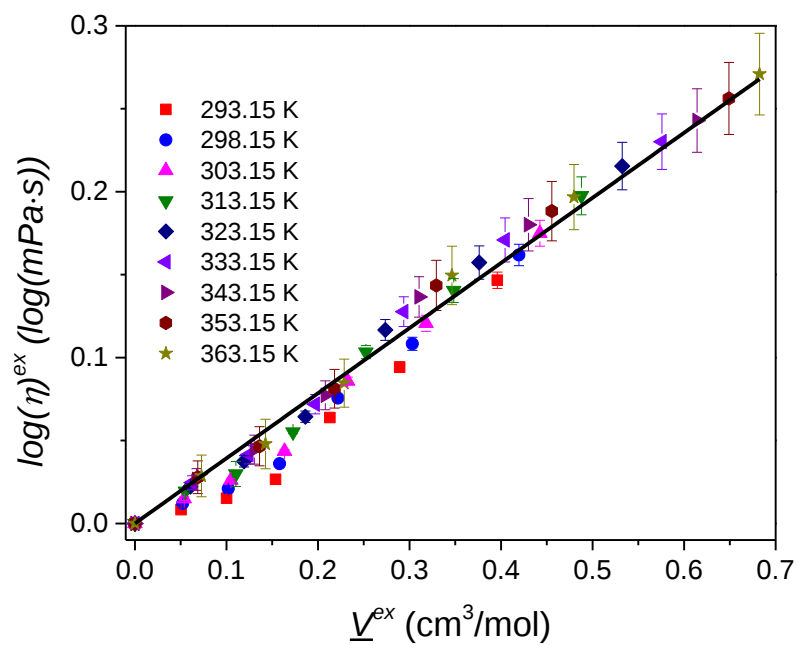


Figure 3.9: The linear correlation between excess log viscosity, $(\log \eta)^{ex}$, and excess molar volume, V^{ex} , of [C₄mim][BF₄] aqueous solution at various temperatures.

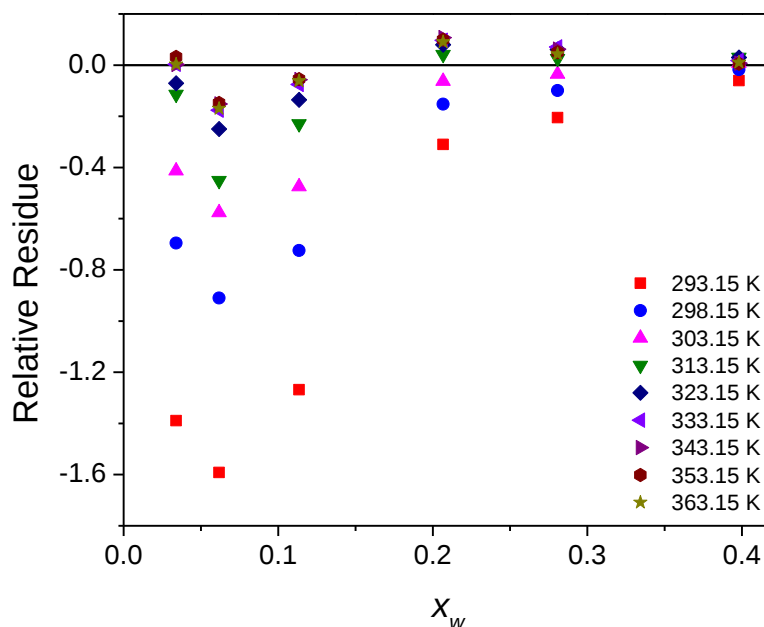


Figure 3.10: The relative residues of excess log viscosity $(\log \eta)^{ex}$ from correlation Equation 3-9 of $[\text{C}_4\text{mim}][\text{BF}_4]$ aqueous solutions at various temperatures and compositions.

Finally, I explore whether this semi-empirical correlation is applicable to aqueous solutions of other ionic liquids. Ionic liquids of similar structures, such as 1-ethyl-3-methylimidazolium tetrafluoroborate ($[\text{C}_2\text{mim}][\text{BF}_4]$) aqueous solutions⁵⁰ are investigated. Their excess molar volume and excess log viscosity are positive for the complete composition, and a linear correlation is evident ($R^2 = 0.809$) for salt-rich regime up to water molar fraction 40% (Appendix A, Figure A.3A). However, this linear correlation does not go through the “zero” point, which suggests an inconsistency in the experimentally reported pure component properties. Indeed, the reported density values for $[\text{C}_2\text{mim}][\text{BF}_4]$ are found to be systemically higher than

those reported by others,⁵¹⁻⁵⁴ which could lead to this offset. For the other imidazolium-based ionic liquids with the common anion $[\text{BF}_4]^-$, such as 1-propyl-2,3-dimethylimidazolium tetrafluoroborate ($[\text{Pdmim}][\text{BF}_4]$),⁵⁵ the excess molar volumes and excess log viscosity are positive for the entire water compositions, and a good linear correlation ($R^2 = 0.959$) is observed for the salt-rich regime (water molar fraction up to 30%) as shown in Figure 3.11A. The density and viscosity of pyridinium-based ionic liquid aqueous solutions have been reported by Mokhtarani *et al.*⁵⁶ In contrast to $[\text{C}_4\text{mim}][\text{BF}_4]$, the excess log viscosity of 1-butylpyridinium tetrafluoroborate ($[\text{BuPy}][\text{BF}_4]$) aqueous solutions are negative for certain water compositions and temperatures in the salt rich regime and no linear correlation between excess molar volume and excess log viscosity is observed for this system (See Appendix A - Figure A.3). However, for the 1-octylpyridinium tetrafluoroborate ($[\text{OcPy}][\text{BF}_4]$), which has a longer alkyl chain, the excess log viscosity is positive for the entire water compositions, and as shown in Figure 3.11B, a good linear correlation between excess molar volume and excess log viscosity of aqueous solution with water molar fraction up to 35% is observed with $R^2 = 0.955$.

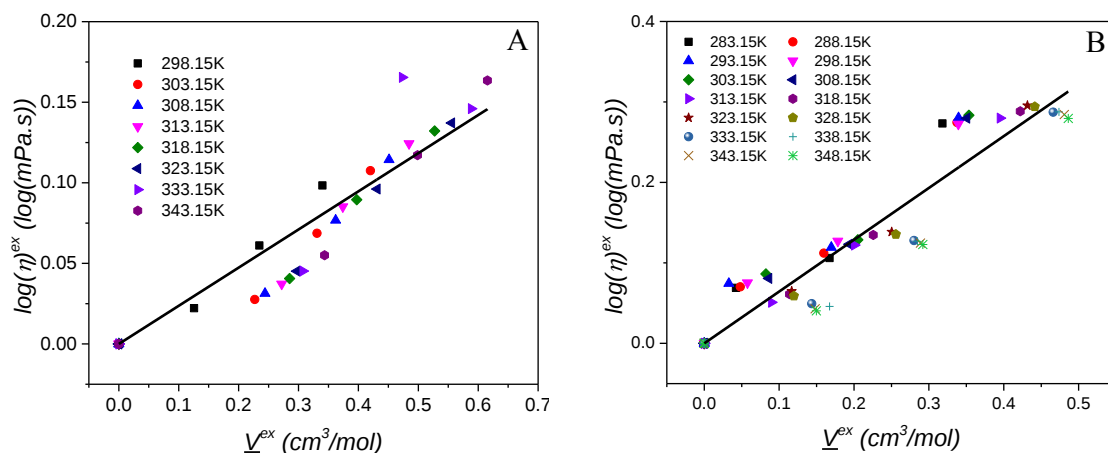
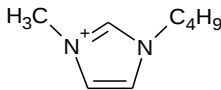
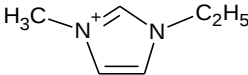
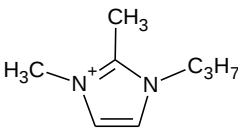
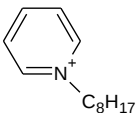
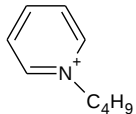
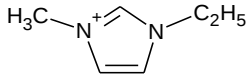
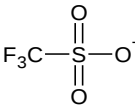


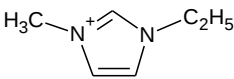
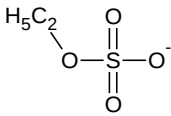
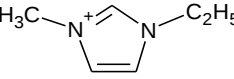
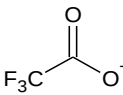
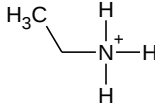
Figure 3.11: The semi-empirical linear correlation between excess log viscosity, $(\log \eta)^{ex}$, and excess molar volume, $\underline{V}^{ex}$, of [Pdmim][BF₄] (A) and [OcPy][BF₄] (B) aqueous solutions in salt-rich regime respectively at various temperatures.

Imidazolium-based ionic liquids aqueous systems with anions other than [BF₄][−] have also been studied. The density and viscosity values for mixtures of water and three ionic liquids: 1-ethyl-3-methylimidazolium ethylsulfate ([C₂mim][EtSO₄]), 1-ethyl-3-methylimidazolium trifluoroacetate ([C₂mim][TFA]), and 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([C₂mim][OTf]) are reported by Rodriguez *et al.*¹⁵ Their excess molar volumes are negative for the entire compositions (*e.g.* [C₂mim][TFA] aqueous solutions) or partial compositions (*e.g.* [C₂mim][EtSO₄] and [C₂mim][OTf]). No obvious linear correlations are observed for these systems (See Appendix A – Figure A.3). The same for the widely used protic ionic liquid ethylammonium nitrate (EAN) water system.⁵⁷ The excess molar volumes change from positive to negative with increasing water content and the semi-empirical

linear correlation between excess molar volume and excess log viscosity cannot be applied to this system.

Table 3.5: Summary of validation of semi-empirical linear correlation between excess log viscosity and excess molar volume of various ionic liquids.

Ionic liquid	Cation structure	Anion structure	$(\log \eta)^{ex*}$	V^{ex*}	Linear correlation	Ref.
1-butyl-3-methylimidazolium tetrafluoroborate ([C ₄ mim][BF ₄])		BF ₄ ⁻	Positive	Positive	Yes	
1-ethyl-3-methylimidazolium tetrafluoroborate ([C ₂ mim][BF ₄])		BF ₄ ⁻	Positive	Positive	Yes [§]	50
1-propyl-2,3-dimethylimidazolium tetrafluoroborate ([Pdmim][BF ₄])		BF ₄ ⁻	Positive	Positive	Yes	55
1-octylpyridinium tetrafluoroborate ([OcPy][BF ₄])		BF ₄ ⁻	Positive	Positive	Yes	56
1-butylpyridinium tetrafluoroborate ([BuPy][BF ₄])		BF ₄ ⁻	Mostly positive	Positive	No	56
1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([C ₂ mim][OTf])			Positive	Mostly positive	No	15

1-ethyl-3-methylimidazolium ethylsulfate ([C ₂ mim][EtSO ₄])			Positive	Mostly negative	No	15
1-ethyl-3-methylimidazolium trifluoroacetate ([C ₂ mim][TFA])			Positive	Negative	No	15
ethylammonium nitrate (EAN)			Mostly negative	Mostly negative	No	57

* The positive or negative values of excess log viscosity, $(\log \eta)^{ex}$, and excess molar volume, V^{ex} of entire water compositions. “Positive” indicates the values are positive for the entire water compositions, and “Mostly positive” indicates the values are positive for most of the water concentration and only for small part of water compositions are negative, “Negative” and “Mostly negative” can be deduced by analogy.

§ Note that the linear correlation does not go through the origin as expected.

The survey of the available literature and our research, as summarized in Table 3.5, shows that this semi-empirical correlation is valid for [C₄mim][BF₄] aqueous solutions and other aqueous solutions of ionic liquids containing the [BF₄][−] anion. The cations include another imidazolium ([Pdmim][BF₄]) and a pyridinium ([OcPy][BF₄]). Note this semi-empirical linear correlation applies only for aqueous ionic liquid solutions in the salt-rich regime ($x_w < 50$ mol%). It is known that the interactions between ionic liquids and water lead to microphase separation and phase inversion for higher water concentrations,^{22, 24-25} which would suggest the model is not applicable.

As summarized in Table 3.5, both the excess molar volume and excess log viscosity must be positive over the entire water composition range of interest for this correlation to apply. The excess properties are determined by the specific interactions

between ions and water molecules.¹⁷ It is reported that anions have the dominant effect on the ionic liquid-water interactions, while water hydrogen bonding with the cations is a secondary effect.¹⁷ The anion [OTf]⁻ (*i.e.*, CF₃SO₃⁻) has a slightly larger water solubility than [BF₄]⁻ group,⁵⁸⁻⁵⁹ and it can form strong acid CF₃SO₃H with the present of proton and react with water molecules to form ion-ligand complex CF₃SO₃⁻ • H₂O or CF₃SO₃⁻ • 2H₂O.⁶⁰ The strength of H-bonding or water solubility increases in the order [BF₄]⁻ < [OTf]⁻, [EtSO₄]⁻ < [NO₃]⁻ < [TFA]⁻.⁵⁹ The water interactions with [OTf]⁻, [EtSO₄]⁻, [TFA]⁻ and [NO₃]⁻ differ from that with [BF₄]⁻, which results in different excess properties that are not captured by our semi-empirical linear correlation. The specific cation plays a secondary effect on the ionic liquids and water molecules interactions, and the cations [Pdmim]⁺, and [OcPy]⁺ have similar hydrophobicity as [C₄mim]⁺, but [BuPy]⁺, and [C₂mim]⁺ are less hydrophobic.⁵⁸ Consequently, this semi-empirical linear correlation is not valid for [BuPy][BF₄] aqueous solutions due to differing cation-water interactions. This empirical survey of the available literature provides hints that the development of a molecular thermodynamic theory for water interactions with ionic liquids in the salt rich regime may be able to predict the broad range of composition specific nonideal behaviors reported to date.

3.3.3 Microstructure of Ionic Liquid Aqueous Solutions

3.3.3.1 Ionic Liquid Micellar Formation

SAXS measurement was taken to evaluate the micellar formation of ionic liquid [C₄mim][BF₄] in water solutions. The absolute intensity of SAXS spectra (scattering intensity, *I*, versus scattering wavevector *q*) of [C₄mim][BF₄] aqueous

solutions with different ionic liquid concentrations at 25 °C are shown in Figure 3.12. For low ionic liquid concentration solutions from 0.2 mol/L to 0.6 mol/L, no significant structure peak is observed over the q range studied. The addition of ionic liquid [C₄mim][BF₄] uniformly increases the overall spectra intensity as expected, due to comparatively higher incoherent scattering of [C₄mim][BF₄]. However, starting from 0.8 mol/L, a slight increase in the intensity at low q range is observed indicating the formation of ionic liquid micellar structure, and the intensity peak become more evident due to the growth of micellar structure as the ionic liquid concentration increases. Because of the amphiphilic structure property of ionic liquid cation [C₄mim]⁺, a structure peak which indicating the formation of micellar structure is expected at higher ionic liquid concentration for ionic liquid aqueous solutions. Thus, the CMC of ionic liquid [C₄mim][BF₄] in H₂O is determined to be 0.8 mol/L by SAXS measurement, which is consistent with previous micellar formation study of [C₄mim][BF₄] aqueous solutions.^{26, 30}

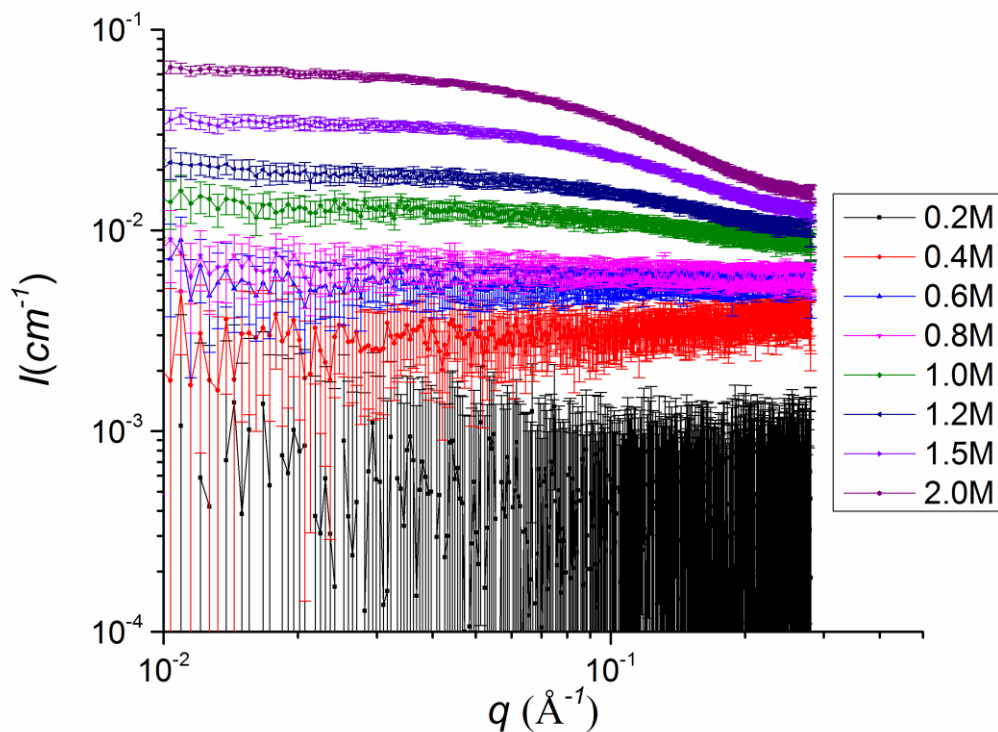


Figure 3.12: SAXS intensity profiles of $[\text{C}_4\text{mim}][\text{BF}_4]$ aqueous solutions (in H_2O) with various ionic liquid contents at 25 °C.

In order to further understand the micellar structure of ionic liquid aqueous solutions, quantitatively accurate model fits of the measured SAXS intensity are used to obtain the shape and size of micellar structure of ionic liquid. Monodispersed sphere form factor model and monodispersed ellipsoid form factor model are used to evaluate the growth of ionic liquid micelle with addition of ionic liquid, and their model fitting results are shown in Figure 3.13. The average size of micellar structure extracted from both of the sphere and ellipsoid form factor models are listed in Table 3.6. As shown in Figure 3.13, for aqueous solution of 0.6 mol/L, there is no scattering

intensity peak at low q value indicating no micellar structure formation, which is confirmed by the negative value of micelle volume fraction extracted from model fitting in Table 3.6. Both of the sphere and ellipsoid model fits are able to capture the intensity peak at low q value for 0.8 mol/L solution as shown in Figure 3.13. The same R_a and R_b values were obtained for the ellipsoid model (same as the radius for the sphere model). This result indicates that the ionic liquid $[C_4mim][BF_4]$ forms spherical micelles with radius of 1.8 nm, which is close to the molecular size of ionic liquid. However, for higher ionic liquid concentration >1.0 mol/L, the sphere model no longer captures the scattering profile and the deviation from a scattering intensity profile increases with ionic liquid concentration. The change of ionic liquid micellar structure shape from sphere to ellipsoid is expected as micelle grows with higher micellar concentration at high ionic liquid concentrations. The growth of ionic liquid micelle with ionic liquid concentration can be illustrated by the volume fraction and size of micelle determined from the ellipsoid model fitting shown in Table 3.6. The volume fraction of ionic liquid micelle in solutions increases, as expected, due to more ionic liquid involving in the formation of micelle at higher ionic liquid concentration. The size of the micellar structure increases with ionic liquid concentration, especially for the R_a direction, size along the R_a direction doubled with ionic liquid concentration increased from 0.8 mol/L to 2.0 mol/L, leaving the size along the R_b direction nearly unchanged. Thus, ionic liquid spherical micelles form initially at 0.8 mol/L and grow along the R_a direction resulting in a “rod” like shape micelle with increasing of ionic liquid concentration.

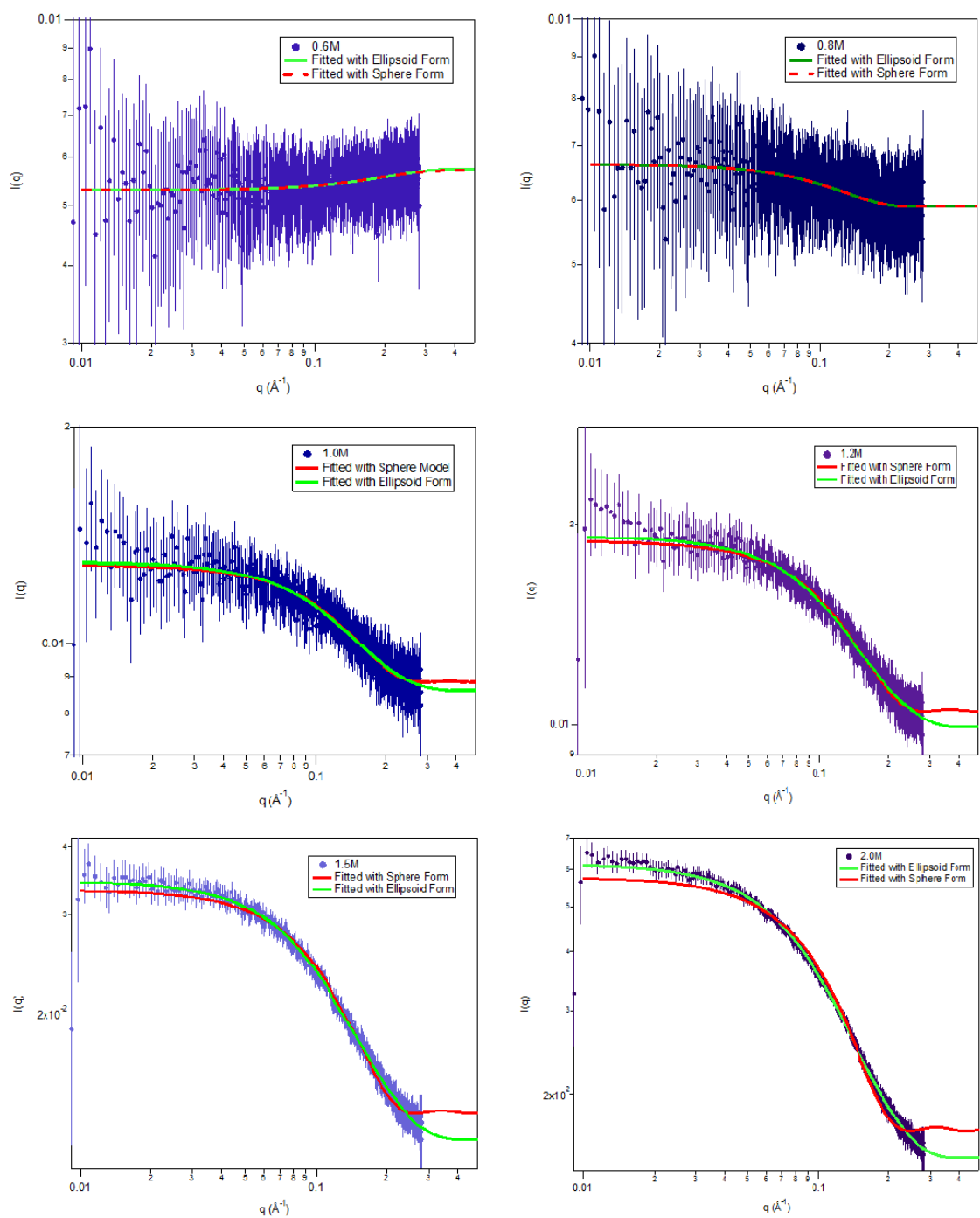


Figure 3.13: The comparisons of sphere and ellipsoid form factor model fittings for SAXS intensity profiles of mixtures of $[\text{C}_4\text{mim}][\text{BF}_4]$ in H_2O at 25°C with ionic liquid concentrations of 0.6 mol/L to 2.0 mol/L.

Table 3.6: Summary of ionic liquid micelle size of [C₄mim][B_F]-H₂O solutions extracted from sphere and ellipsoid form factor model fittings.

[C ₄ mim][B _F] concentration mol/L	Sphere model fitting		Ellipsoid model fitting		
	Volume fraction	<i>R</i> nm	Volume fraction	<i>R_a</i> nm	<i>R_b</i>
0.6	-1.7×10 ⁻⁴	---	-2.3×10 ⁻⁴	---	---
0.8	8.4×10 ⁻⁵	1.8	8.4×10 ⁻⁵	1.8	1.8
1.0	0.7×10 ⁻³	1.6	1.0×10 ⁻³	2.3	1.1
1.2	1.3×10 ⁻³	1.6	2.2×10 ⁻³	2.5	1.0
1.5	2.6×10 ⁻³	1.7	4.7×10 ⁻³	2.9	1.0
2.0	4.3×10 ⁻³	1.8	7.0×10 ⁻³	3.3	1.2

3.3.3.2 Water Cluster Formation

Absolute SANS spectra (scattering intensity, *I*, versus scattering wavevector *q*) for varying water compositions at 25 °C are shown in Figure 3.14. The pure ionic liquid and [C₄mim][B_F]/D₂O solutions with water content up to 11 wt% (0.60 D₂O mole fraction) show no significant structure over the *q* range studied. A slight increase is observed towards higher *q* values consistent with the expected molecular structure in the ionic liquid⁶¹ and the addition of D₂O uniformly lowers the overall spectra, as expected, because D₂O has comparatively lower incoherent scattering. For aqueous solution of 15 wt% D₂O content (0.67 mole fraction), there is a slight decrease in intensity for higher *q* (*q* = 0.4~0.5 Å⁻¹), which is indicative of water association. However, this intensity change is not significant enough to enable reliable determination of water association from model fitting. A significant change in SANS intensity is evident starting at 20 wt% D₂O content (0.74 D₂O mole fraction), whereby the relative growth of scattering intensity at low *q* signals the onset of microstructure formation in the mixtures on length-scales greater than the molecular size of the

constituents. Further addition of water leads to large increases in scattering intensity at lower q values, consistent with the formation of larger, nanoscale structures.

These observations help explain previous experimental results²⁴⁻²⁷ and verify simulations,²²⁻²³ which can be analyzed as follows. For low water concentrations, water molecules are incorporated into the ionic liquid cation-anion network without significantly disrupting the structure.²² Katayanagi *et.al.*⁶² measured the excess chemical potential, μ_i^E , the excess partial molar enthalpy, H_i^E , and excess partial molar entropies, S_i^E in [C₄mim][BF₄]-H₂O system at 25 °C. They found that H_{IL}^E and S_{IL}^E of [C₄mim][BF₄] are almost zero with the net μ_{IL}^E also zero in the IL-rich region, $x_{IL} > 0.5-0.6$. These results reveal that the structure of the ionic liquid is not disrupted by the addition of small amounts of water. Furthermore, homogeneous mixing was proposed in the [C₄mim][BF₄]-H₂O mixture in the salt mole fraction range of 0.4 - 1 by Almasy³⁰ and confirmed using concentration fluctuations from vapor pressure measurements.³⁰ However, for water addition beyond the IL-rich boundary (around $x_{IL} = 0.4$), the ions are fully hydrated and excess water molecules aggregate and form distinct water clusters. The mixture phase transforms from IL-rich to water-rich mixture beyond this concentration.^{22, 30} Water aggregation and cluster formation were also observed by MD simulations.²²⁻²³ Our SANS scattering intensity profiles of 20 wt% water concentrations and above confirm the formation of distinct nanostructures. The relatively high molar water concentration required for nanocluster formation is consistent with the propensity of water to associate with the ionic groups in the IL.

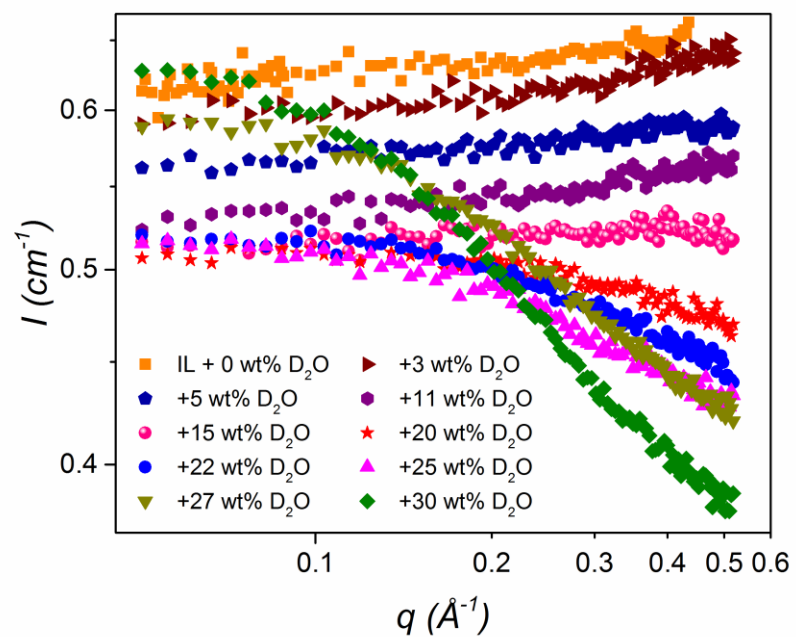


Figure 3.14: SANS profiles of mixtures of [C₄mim][BF₄] and D₂O at 25 °C.

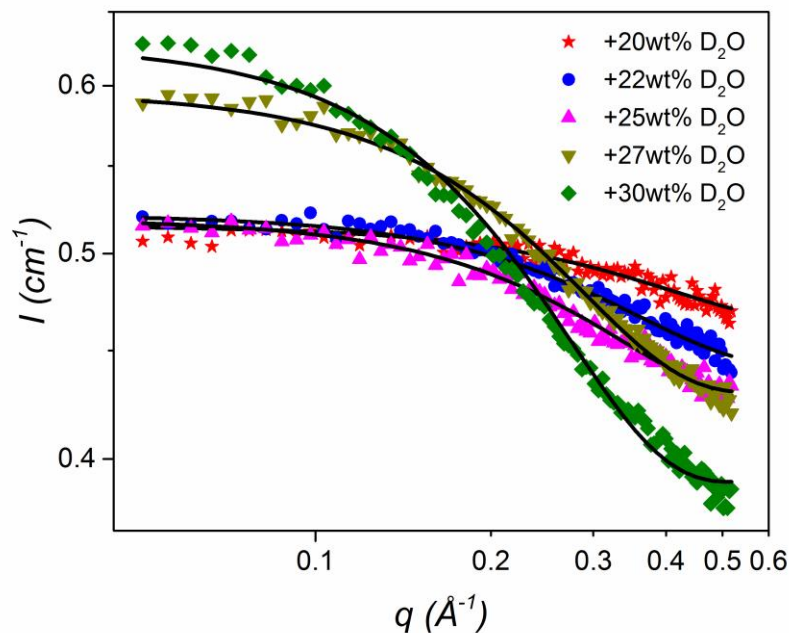


Figure 3.15: SANS profiles and model fitting for mixtures of $[\text{C}_4\text{mim}][\text{BF}_4]$ and D_2O at 25 °C for higher D_2O concentrations.

Quantitatively accurate model fits of the measured SANS intensity are shown in Figure 3.15. The radius and volume fraction, ϕ_{cluster} , of water clusters are determined through model fitting, and these parameters are summarized in Table 3.7. The measured scattering intensities are fitted to a monodisperse, sphere form factor, with the water cluster size, r_{cluster} , volume fraction, ϕ_{cluster} , and scattering length density of solvent, $\text{SLD}_{\text{solvent}}$, allowed to vary within constraints. In the fitting, the volume fraction of the D_2O clusters is restricted by mass balance that accounts for the fraction of the D_2O that is dissolved in molecular form in the ionic liquid, such that only the excess D_2O is available to form clusters. The scattering length density of the solvent is constrained within the range of the SLD of pure ionic liquid $[\text{C}_4\text{mim}][\text{BF}_4]$.

In the fitting procedure, the D₂O mass balance is enforced to select a unique fit. From these fits, I extract the average D₂O cluster size and volume fraction as shown in Table 3.7. In this manner, SANS provides a method to quantitatively measure the molecularly dissolved D₂O and the amount that forms distinct nanoclusters, along with the size of these clusters.

Table 3.7: Summary of D₂O water distribution in water dissolved state and microphase separated state for mixtures of [C₄mim][BF₄] and D₂O for water contents above 20 wt% at 25 °C.

Properties	IL+20 wt%	IL+22 wt%	IL+25 wt%	IL+27 wt%	IL+30 wt%
$x_w (total)^a$	0.74	0.76	0.79	0.81	0.83
$\phi_w (total)^a$	0.21	0.24	0.27	0.29	0.32
$\phi_{cluster}^a$	0.043	0.045	0.048	0.053	0.063
$r_{cluster} (\text{\AA})$	5.5	6.4	6.8	8.2	8.9
$\phi_w^s (in\ dissolved\ state)^b$	0.18	0.20	0.23	0.25	0.28
$SLD_{dissolved\ phase}$	2.29×10^{-6}	2.40×10^{-6}	2.54×10^{-6}	2.66×10^{-6}	2.79×10^{-6}
$x_w^s (in\ dissolved\ state)^b$	0.69	0.72	0.76	0.78	0.80
$x_w^s / x_{IL} (in\ dissolved\ state)^b$	2.3	2.6	3.1	3.5	4.0

^a $x_w (total)$, $\phi_w (total)$, $\phi_{cluster}$, and ϕ_w^s are the molar fraction or volume fraction of total water, water cluster or dissolved water in the system.

^b $\phi_w^s (in\ dissolved\ state)$, $x_w^s (in\ dissolved\ state)$, and $x_w^s / x_{IL} (in\ dissolved\ state)$ are the water and ionic liquid distribution in the molecularly dissolved state

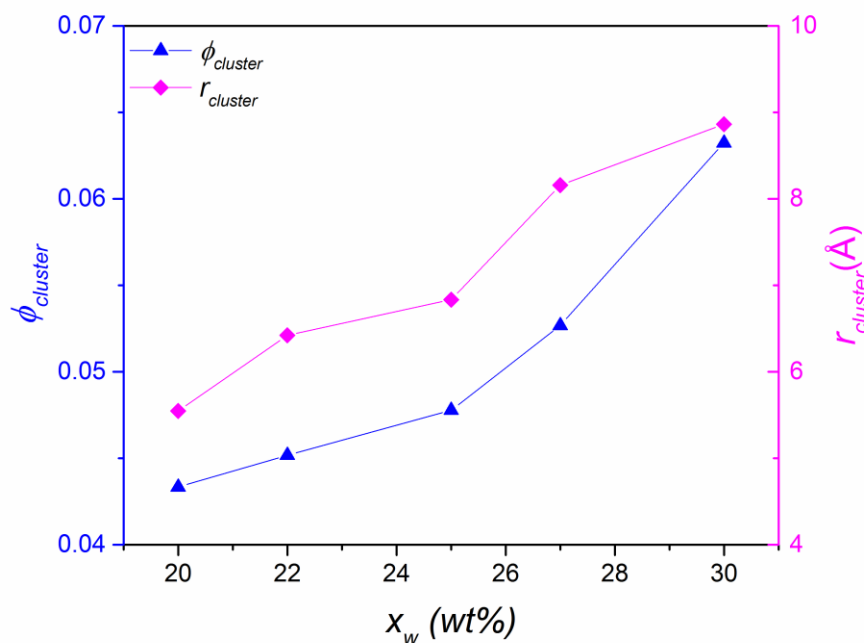


Figure 3.16: The volume fraction and size of D₂O clusters as a function of the overall D₂O weight fraction for [C₄mim][BF₄] and D₂O mixtures at 25 °C.

The D₂O cluster size, r , and volume fraction, ϕ , extracted from SANS fitting are plotted in Figure 3.16. The D₂O cluster size and volume fraction both increase with overall D₂O mole fraction for D₂O content of 20 wt% (0.74 D₂O mole fraction) and above, and this behavior is in reasonable quantitative agreement with molecular dynamic simulations.²² Indeed, the simulations of Liu *et.al.*²² suggest water nanoclusters with a well-defined structure, as opposed to weak aggregates, only exist for water mole fractions of ~70% and above, and that the aggregation number increases with increasing water content until the water percolates the material. Furthermore, at 70 mole% the average aggregation number is ~160 water molecules, which corresponds to a droplet of water of approximately 10 Å in radius. Our

experimental observations show well-defined water clusters above 70 mole% that are about half the average radius as predicted. These clusters have properties consistent with those of inverse microemulsions, but are novel in that they are present in a binary mixture, consistent with the surfactant-like properties of ILs. Some of the deviation in the simulation prediction may be due to the simulations showing a very broad size distribution that approaches the limited size of the simulation box, or may be specific to isotope effects. Nevertheless, the trends in the simulations are in good qualitative agreement with our experimental observations.

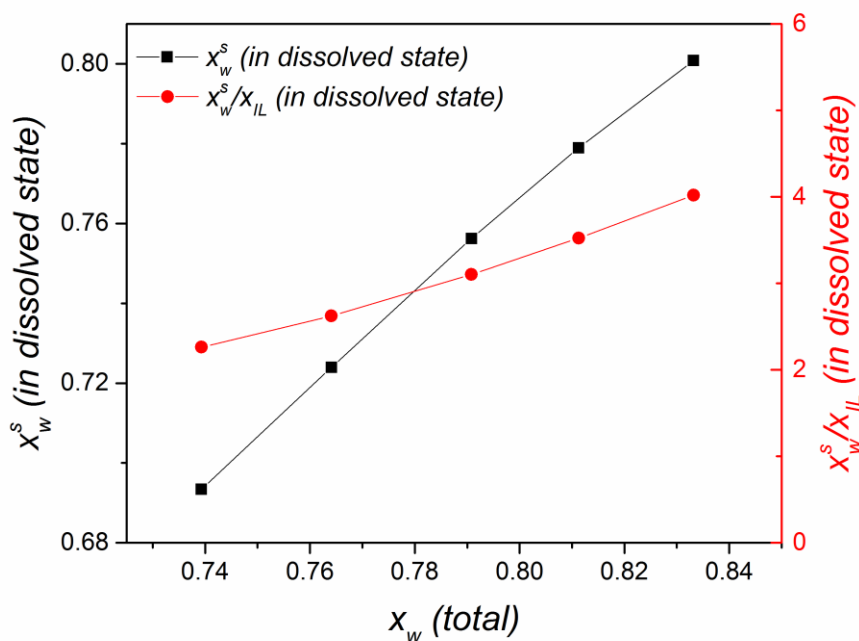


Figure 3.17: Mole fraction of dissolved D₂O and the molar ratio of dissolved D₂O to ionic liquid as a function of total D₂O mole fraction for mixtures of [C₄mim][BF₄] and D₂O at 25 °C.

SANS measurements enable measurement of the distribution of D₂O between being molecularly dissolved and microphase separated in the mixtures with [C₄mim][BF₄]. These distributions are summarized in Table 3.7 and plotted in Figure 3.17 as mole fractions and mole ratios. The volume fraction of D₂O cluster, $\phi_{cluster}$, shown in Table 3.7 was obtained from SANS model fitting, the constraint of mass balance for the D₂O and Equation 3-1. The mole fraction water distributions were calculated based on the volume fraction of water in the molecular dissolved state and cluster microphase separated state. As seen in Table 3.7, the volume fraction of dissolved D₂O, ϕ_w^s , increases slightly with added D₂O, along with the growth of D₂O clusters. This indicates that D₂O partitions between the molecularly dissolved state and the microphase separated state, and both of these increase nearly linearly with added D₂O, as evident in Figure 3.17.

Returning to the lower D₂O concentrations, the data shows that D₂O molecularly dissolves in the ionic liquid. Complementary measurements of the viscosity and density⁴⁻⁶ of mixtures show significant non-idealities, which is consistent with a specific interaction of the water with the ionic groups. Such hydration at low water content has been confirmed by experiments²⁴⁻²⁷ and simulations.²²⁻²³ Shirota *et al.*²⁵ investigated the state of molecular association in [C_nmim][BF₄]-H₂O by Raman spectroscopy and showed that the symmetric F-B stretching mode of [BF₄]⁻ in the [C_nmim][BF₄]-H₂O shifts to higher frequency with increase water concentration, indicating hydrogen bonding between water and the anions. This experimental observation is consistent with molecular dynamic (MD) simulations by Moreno *et al.*²³ Three dimensional probability distribution of water around [C₄mim]⁺ cation, as simulated through MD by Liu *et al.*,²² indicates

interactions between water and the cation as well. However, due to the asymmetry and larger size of the cation, the correlation between the cation and water is found to be weaker than that between water and the anion.²² This was also confirmed by experiment as well as predicted using UNIFAC and COSMO-RS models for gas solubility in ionic liquids.^{3, 44} Furthermore, water was found to interact with the anions by bridging between anions. As the $[\text{BF}_4]^-$ anion has four fluorine atoms and water has two hydrogens, the coordination ratio is 2:1 for water/IL for full hydration as illustrated in Figure 3.17. As seen in Figure 3.14, water clusters are evident in the SANS spectra for water content above 15 wt% (0.67 mole fraction), consistent with this interpretation. Figure 3.17 shows that this corresponds to a mole ratio of about 2:1 for the molecular dissolved D_2O in the ionic liquid as determined by SANS, which is quantitatively consistent with this molecular interpretation.

Taib *et al.* measured the density of $[\text{C}_4\text{mim}][\text{BF}_4]$ aqueous solutions at 25 °C of full water concentration range and plotted the excess molar volume as a function of water molar fraction in Figure 6 of reference⁶, which is consistent with the earlier data reported by Ries *et al.*⁴ The excess molar volume of $[\text{C}_4\text{mim}][\text{BF}_4]$ aqueous solution is positive and increases with addition of water due to the volume expansion caused by ordered hydrogen bonds between water and anions. However, the excess molar volume reaches a maximum value at water mole fraction of 0.6~0.7, and then decreases monotonically with the addition of more water. This maximum in excess molar volume at 0.6~0.7 water mole fraction is consistent with the phenomenon of water cluster formation as revealed by our SANS measurements. At 0.6~0.7 water mole fraction, water clusters start to form and grow with D_2O addition as seen in Figure 3.17. This added water is in the form of microphase separated water clusters,

which is in the form of bulk water and hence, the overall mixture excess molar volume will decrease. The fraction of bulk water (water cluster) continually increases with addition of water, as shown in Table 3.7, resulting in the continued decrease of the apparent excess molar volume for this microphase separated mixture. In summary, our SANS measurements confirm the mechanism whereby water addition to this ionic liquid leads to significant non-idealities in mixture thermophysical and transport properties, *e.g.* mixture density and viscosity, in the salt-rich regime due to this strong association between water and the $[\text{BF}_4]^-$ anion.

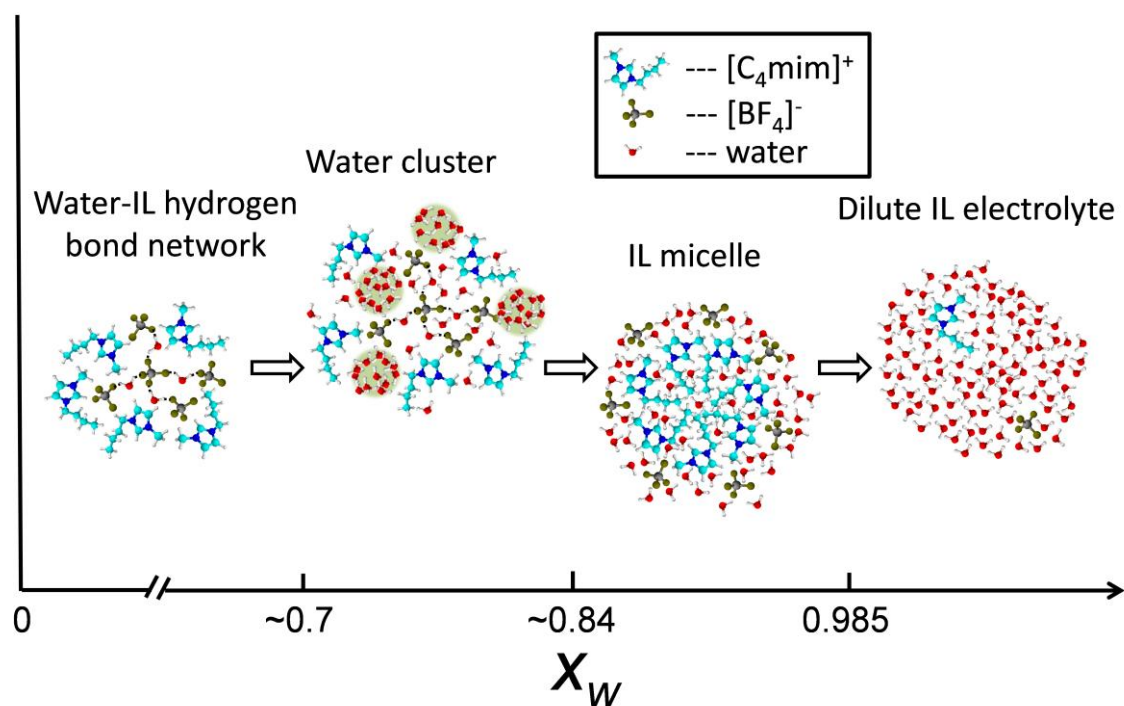


Figure 3.18: The schematic illustration of structures in mixtures of $[\text{C}_4\text{mim}][\text{BF}_4]$ and D_2O .

With this compilation of literature data, simulations and the new microstructural measurements presented here, a coherent picture emerges for the microphase solution structure in $[\text{C}_4\text{mim}][\text{BF}_4]$ water mixtures over the entire composition range, as illustrated in Figure 3.18. Water is soluble in the ionic liquid until ~ 2 water molecules per ionic liquid ion pair, whereupon microphase separation of water is observed. The addition of water to ionic liquid $[\text{C}_4\text{mim}][\text{BF}_4]$ above ~ 80 mole % results in water percolation.¹⁵ Above this concentration, there is a phase inversion and the IL forms aggregates consistent with its amphiphilic character. This conventional cationic surfactant-like behavior has been well studied.^{4, 22, 26-28, 30, 62} At $x_w = 0.925$ SANS³⁰ and vapor pressure measurements³⁰ indicates the most significant micellization of the ionic liquid, in agreement with MD simulation.²² The strong concentration fluctuations suggest that the system is quite close to a de-mixing spinodal at this composition.³⁰ The critical aggregation concentration (CAC) or the critical micellar concentration (CMC) of $[\text{C}_4\text{mim}][\text{BF}_4]$ in this water-rich regime was determined to be $x_w = 0.985$ through vapor pressure,⁶² surface thermal coefficient,²⁷ surface tension,²⁰ SANS,^{26, 30} conductivity,^{4, 26} NMR²⁸ and fluorescence spectroscopy²⁸ measurements. For water concentrations beyond this critical concentration, the ionic liquid dissociates in the water as dilute electrolyte solution.

3.4 Conclusions

The densities and viscosities of binary mixtures of 1-butyl-3-methylimidazolium tetrafluoroborate ($[\text{C}_4\text{mim}][\text{BF}_4]$) with water are reported for the temperature range of 283.15 to 373.15 K over the salt-rich composition regime. Excess molar volumes and non-idealities of the viscosities are calculated and can be accurately correlated, which are provided for reference. A new semi-empirical correlation between the excess

mixture viscosities and the excess molar volumes in the salt-rich regime is identified, which is consistent with free volume theory. This correlation enables predicting the viscosity of ionic liquids with added water directly from density measurements, and is also found to be valid for other ionic liquids aqueous solutions with similar ion structures. A survey of the literature identifies ionic liquids for which this correlation is valid, and provides evidence for the role of specific molecular interactions that govern the observed non-idealities in salt-rich aqueous solutions of ionic liquids.

Micellar formation of ionic liquid [C₄mim][BF₄] in aqueous solution is investigated through SAXS measurements. The CMC of [C₄mim][BF₄] in H₂O is determined to be 0.8 mol/L, which is consistent with previous literature results.^{26, 30} Spherical micelles form at ionic liquid concentrations above CMC; however, micelles grow to ellipsoid rod shape as ionic liquid concentration increases. A “rod” like micellar structure is observed at higher concentration.

A microphase transition to water nanoclusters resembling an inverse microemulsion is observed in the salt-rich regime of mixtures of the room temperature ionic liquid [C₄mim][BF₄] with the addition of D₂O above ~ 70 mol%. This transition is consistent with previous reports on related ionic liquid mixtures as also deduced from SANS measurements, vapor pressure, NMR, Raman, IR spectroscopy measurement, and dynamic molecular simulation. In the IL-rich region, water molecules are isolated and accommodated in the ionic liquid cation-anion polar network by interacting with anions and cations through hydrogen bonds. Such mixtures are a homogenous solution, with no significant changes in microstructure upon water addition as detected by SANS measurement. Water form clusters when the water/ionic liquid molecular ratio exceeds ~ 2:1, as expected from molecular

structure determination. Distinct nanometer-sized water clusters form and grow with water content, and water continues to partition between the dissolved state and microphase separated state. These observations complement measurements of water-continuous mixtures to complete a picture that displays microphase separation and phase inversion in this binary mixture which shows similarities to that of traditional oil-water-surfactant systems. These microstructure measurements of water dissolution in the salt-rich regime also confirm proposed mechanism for the observed non-idealities in mixture thermophysical and transport properties such as density and viscosity.

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Chapter 4

PARTICLE SYNTHESIS AND CHARACTERIZATION

The purpose of this chapter is to describe the materials and the protocol used to synthesize fluorocarbon coated silica particles. The particle properties, such as the chemical coating on particle surface, particle size, and density, will be discussed in this chapter. Text and figures are reproduced and adapted with permission from Gao J., et al. *ACS Nano* 2015, 9, (3), 3243-3253.

4.1 Materials and Methods

Colloidal silica nanoparticles (NexSil 125-40, nominal radius 42.5 nm) were purchased from Nyacol Nano Technologies, Inc. and used as received (40 wt% solid in H₂O with sodium stabilizing counterion). Fluorocarbon 1H,1H,9H hexadecafluoro-1-nanol (CAS 376-18-1, C₉H₄F₁₆O) was selected for surface modification for the silica particles (Figure 4.1). The ionic liquid [C₄mim][BF₄] (Iolitec, >99% pure) was dehydrated at 70 °C under vacuum condition for 24 h prior to use. The final water content was 373 ppm as determined by the Karl Fischer titration. The basic information of chemicals used in particle synthesis and characterization are listed in Table 4.1.

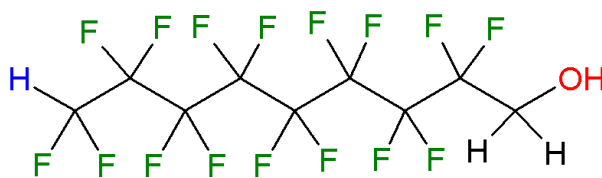


Figure 4.1: Chemical structure of fluorocarbon 1H,1H,9H hexadecafluoro-1-nonanol used to functionalize the particle surface.

Table 4.1: Summary of chemicals used in particle surface coating and characteristics.

Materials	Manufacturer	Purity
NexSil 125-40	Nyacol	40 wt% solid in H ₂ O
1H,1H,9H hexadecafluoro-1-nonanol	Matrix Scientific	97%
[C ₄ mim][BF ₄]	Iolitec	99%
Ethanol	Decon	200 proof
Sulfuric acid	Fisher Chemical	98%
deuterated chloroform (CDCl ₃)	Fisher Chemical	99.9%

After coating procedure, the surface chemical on the silica particle was confirmed by proton nuclear magnetic resonance (¹H NMR). ¹H NMR spectra were measured on a Bruker AV400. Uncoated silica particles, fluorinated silica particles, and fluorocarbon 1H,1H,9H hexadecafluoro-1-nonanol were dissolved in deuterated chloroform (CDCl₃) separately before measurements. MestReNova NMR software was used to perform spectra analysis.

The grafting density of fluorocarbon on the silica particle surface was measured by thermogravimetric analysis (TGA) using a TA Instruments Q500. Nitrogen gas was flowing through the sample pan over the entire measurement. The temperature increased from 25 °C to 80 °C at a rate of 10 °C/min and equilibrated at 80 °C for 20 min to remove physically adsorbed water. Then, the temperature was

increased to 900 °C at the same rate as before and equilibrated at 900 °C for 15 min to ensure the complete decomposition of coated fluorocarbon.

A high resolution SEM (JSM-7400F) was used to image the dried silica particles, their size distributions were analyzed through ImageJ software.¹ To prepare for SEM imaging, a dilute suspension ($\phi = 0.001$) of silica particles was pipetted onto the alumina stubs, allowing it to completely dry by atmosphere air. Then, the dried samples were sputter coated with an Au/Pd layer under vacuum for 40 s before being loaded into the SEM chamber and digital images were recorded.

The diffusivity of uncoated silica particles and coated silica particles suspension in various solvents were measured using a Brookhaven Instruments ZetaPals dynamic light scattering (DLS). Dilute (0.1 wt%) particle dispersions were used for DLS measurements. Single particle size was determined from diffusion coefficient measured using Stokes-Einstein-Sutherland correlation²⁻³ as described in Chapter 2.

Small Angle Neutron Scattering (SANS) measurements were performed for the dilute silica particle dispersions ($\phi = 0.004$) at the National Institute of Standards and Technology (NIST) Center for Neutron Research (NCNR) in Gaithersburg, MD on the NG7 beamline. Samples were loaded into demountable titanium cells with a 1 mm path length. Three different detector distances: 1m, 4m, and 13m were used to probe the complete length scale. Scattering intensities were reduced to absolute scale⁴ and analyzed following the protocol described in Chapter 2.

The densities of dispersions were measured using an Anton Paar DMA-4500M densitometer. Particle density in solution was extracted from a series of six diluted concentrations with particle mass fraction $0 \leq x < 0.02$. For the uncoated silica, the

stock NexSil solution ($x = 0.415 \pm 0.006$) was diluted with a solution of 0.1 mM NaCl nanopure H₂O solution ($\text{pH} = 9.1 \pm 0.1$) to maintain particle stability and match the mother liquid. The fluorocarbon-coated silica was dispersed into [C₄mim][BF₄], a good solvent for the fluorocarbon brush. Assuming ideal mixing of the dispersion constituents, the particle density can be calculated using the following equation based on ideal mixing:⁵

$$\frac{1}{\rho_{\text{solution}}} = \left(\frac{1}{\rho_{\text{particles}}} - \frac{1}{\rho_{\text{solvent}}} \right) x + \frac{1}{\rho_{\text{solvent}}} \quad 4-1$$

where, ρ_{solution} , $\rho_{\text{particles}}$, and ρ_{solvent} are the solution density, particle density, and solvent density, respectively; x is the mass fraction of particles in solution.

4.2 Particle Synthesis

The 9-carbon chain fluorocarbon 1H,1H,9H hexadecafluoro-1-nonanol was covalently grafted to the nanoparticle surface *via* a dehydration reaction following the protocol of van Helden *et al.*⁶ According to literature, a model adhesive hard sphere (AHS) particle was synthesized using this procedure to chemically graft 1-octadecanol chain layer onto the surface of silica particles.⁷ Thus, a similar coating protocol was used for the fluorocarbon coating system. The main chemical reaction during the surface coating is the dehydration reaction between silanol group on the surface of silica particle and the hydroxyl group at the end of the fluorinated alcohol chain (*i.e.* -Si-OH + R-OH $\rightarrow$ -Si-O-R + H₂O), whereas, other side chemical reactions such as -Si-O-Si- + R-OH $\rightarrow$ -Si-O-R + Si-OH and -Si-O-Si- + H₂O $\rightarrow$ 2-Si-OH (in which -R is fluorinated hydrocarbon), can also happen depending on the silica particle surface chemistry.⁸⁻⁹

Colloidal silica nanoparticles NexSil 125-40 were used for surface coating and the surface coating procedure is shown in Figure 4.2. First, 40 g of the 40 wt% silica particle suspension was poured into a beaker (250 mL) and agitated with a magnetic stirring bar. Four drops of sulfuric acid were added to the particle suspension while stirring to induce protonation of the silica surface, promoting the dehydration chemical reaction. The mixture was stirred for 15 min to ensure a homogenous solution was reached. Then, 70 g of ethanol was added into the mixture solution under stirring in order to help the dissociation of the H^+ from the surface of particle. The mixture was stirred for 15 min followed by a DLS measurement of particle size to ensure the silica particles were well dispersed in this mixture. After that, 13 g of fluorocarbon 1H,1H,9H hexadecafluoro-1-nonanol was added into a separate round bottom flask. Then, 156 g ethanol was added into the flask, and the mixture was stirred for 5 min to dissolve the fluorocarbon. After complete dissolving, all the materials in the beaker are transferred into the round bottom flask slowly under stirring.

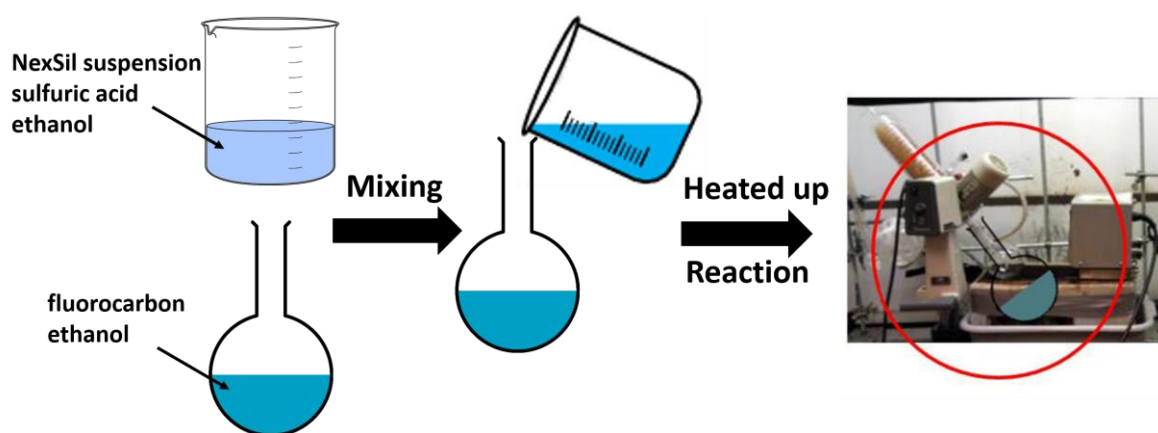


Figure 4.2: A schematic flow chart of the particle coating procedure.

The round bottom flask contained the fluorocarbon, NexSil silica particle suspension, ethanol, and sulfuric acid was mounted onto a rotary evaporator (RE211 from Buchi), shown in Figure 4.3. The round bottom flask was immersed into an oil bath with a high-precision temperature control system. Rotary evaporator condenser with 15 °C circulating cold water was used to condense the water and ethanol vapor, which was then collected into a separate flask. The mixture solution was heated up to 70 °C and equilibrated for 15 min in oil bath. Then the temperature was raised up to 222°C by 10 °C every 15 min. During this process, the mixture started to boil off when the temperature reached 90 °C and then condensation of water/ethanol vapor mixture was observed at 100~110 °C. After the temperature reached to 222 °C, the reaction was allowed to proceed for 5 h at this temperature, after which, the round bottom flask was lifted up from the oil bath and allowed to cool down to room temperature overnight.

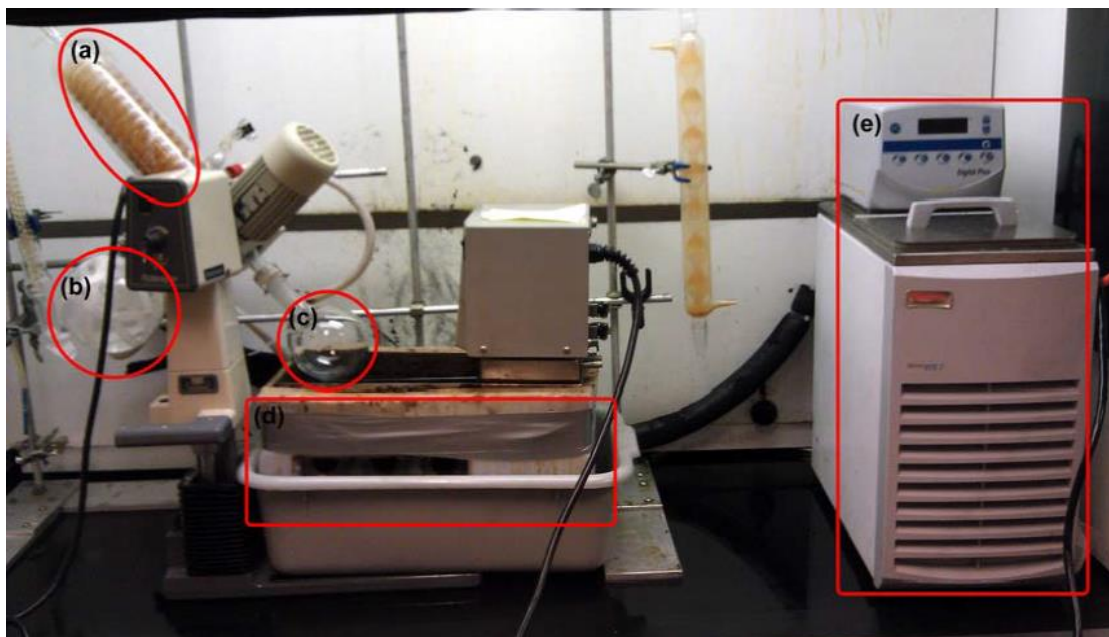


Figure 4.3: The experimental apparatus for the particle surface coating, consisting of a rotary evaporator and a heating oil bath. (a) Condenser to cool down evaporated water and ethanol, (b) collection flask to collect water/ethanol condensation, (c) reaction flask, (d) oil bath, and (e) condenser cooling water. Image courtesy of Dr. Jung Min Kim.

After the reaction, the mixture was cooled down to the room temperature. The obtained silica particle “cake” at the bottom of reaction flask was dispersed in ethanol using water bath sonication for 2 h. After ensuring all the particles were well dispersed, and no particle agglomerates left, the particle suspension was centrifuged at 7500 g_s (g_s is the standard gravitational acceleration) for 1.5 h using a Sorvall RC6+ centrifuge. After the centrifugation, the supernatant liquid was discarded. The particle sediment “cake” was dispersed in fresh ethanol again in a glass bottle under sonication until all the particles were dispersed. Then, another centrifugation was performed. This cleaning procedure was repeated 3 times to make sure all the excess

fluorocarbon was removed by ethanol. Finally, the cleaned particles were stored in ethanol until use and no visual sedimentation was observed, even after 4 months.

To prepare dispersions of the fluorocarbon coated silica particles, concentrated coated particle dispersion in ethanol was dried by evaporating ethanol using a nitrogen flowing stream for 4 h at room temperature. Then, the dried silica particles were placed under vacuum at -30 inHg for 24 h to remove the residual ethanol and ready to be used to prepare particle dispersions in various solvents including ionic liquids.

4.3 Particle Characterization

The properties of single silica particle before and after coating, such as surface coating chemical, particle size, and density, have been evaluated and characterized through various methods. The successful grafting of fluorocarbon onto the silica particle surface is confirmed by ^1H NMR and the grafting density is measured by TGA. The size distributions of dried uncoated and coated silica particles are investigated using SEM. The hydrodynamic radii of uncoated and coated silica particles dispersed in various solvents are measured and compared using different techniques, such as DLS and SANS. The skeletal particle densities in solutions at room temperature are evaluated for both uncoated and coated particles using densitometer.

4.3.1 Surface Coating

4.3.1.1 Proton Nuclear Magnetic Resonance (^1H NMR)

The ^1H NMR spectra of uncoated silica particle, fluorocarbon coated silica particle and fluorocarbon 1H,1H,9H hexadecafluoro-1-nonanol suspended in deuterated chloroform (CDCl_3) are shown in Figure 4.4. Compared with the uncoated

silica particles, the NMR spectrum of the fluorocarbon coated silica particles shows chemical shift peaks at 4.1 ppm and 5.9-6.2 ppm, which corresponds to the chemical shift peaks of fluorocarbon, indicating the success of coating fluorocarbon onto the surface of silica particles through covalent bonding.

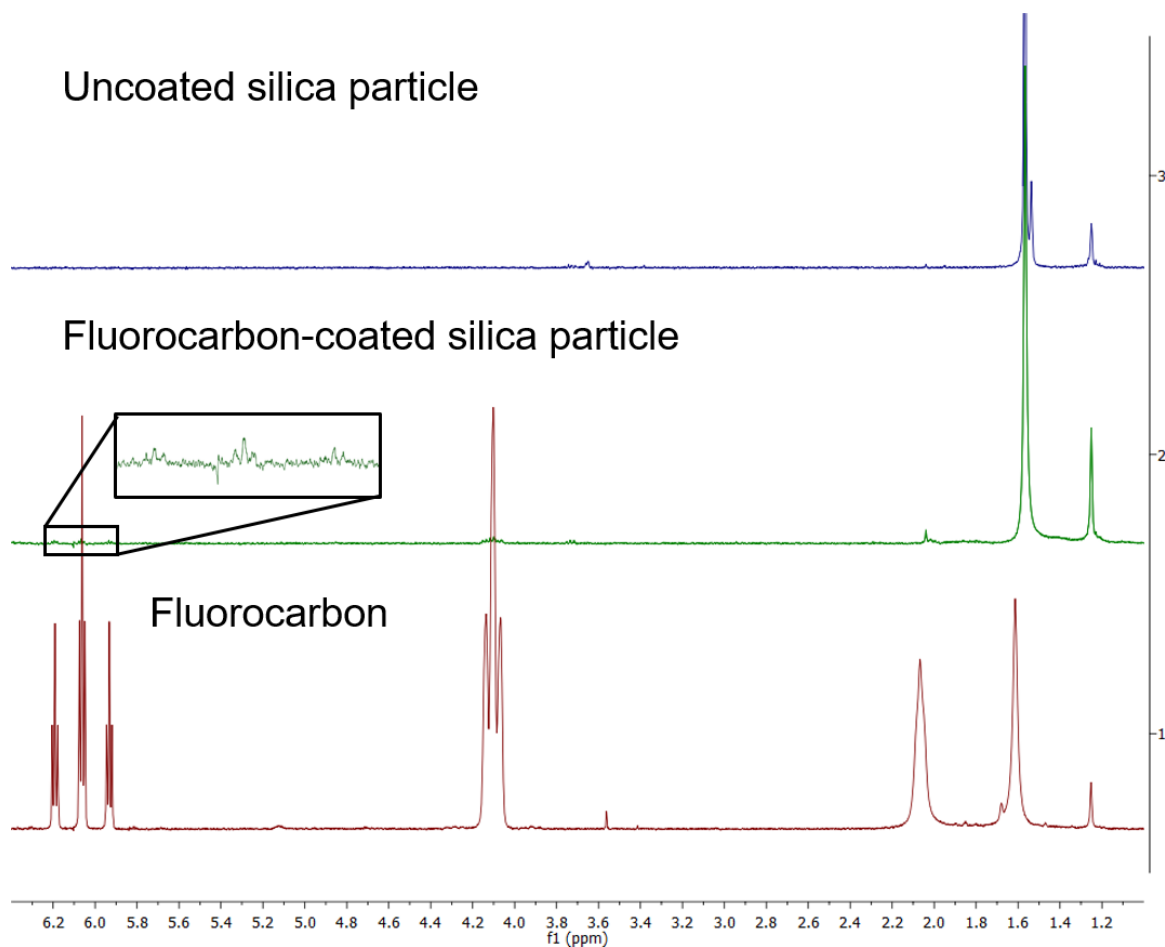


Figure 4.4: ^1H NMR spectra of uncoated silica particles (top), fluorocarbon coated silica particles (middle), and 1H,1H,9H hexadecafluoro-1-nonanol (CAS 376-18-1, $\text{C}_9\text{H}_4\text{F}_{16}\text{O}$) (bottom) in CDCl_3 .

4.3.1.2 Thermogravimetric Analysis (TGA)

The grafting density of fluorocarbon onto particle surface is measured by TGA. The TGA results of uncoated and coated silica particles are shown in Figure 4.5 in the form of mass fraction versus temperature. The uncoated particles show a weight loss of about 2.3 wt%, which is attributed to the desorption of physically adsorbed water. The coated particles have a weight loss of about 4.5 wt %, which indicates the additional presence of the surface modifier. From this weight loss, the graft density is calculated to be 1.4 chain/nm² of particles based on a particle average radius of 54.2 nm obtained by SANS. This value is lower than the graft density for octadecyl alcohol (2.9/nm²) reported previously.¹⁰ It is calculated that 28-35% surface silanol groups are covalent bonded with fluorinated group based on the estimation of 4-5 silanol group/nm².⁹ This lower graft density is attributed to the larger molecular size of the fluorinated compound. The calculated graft density corresponds to ~ 60 % of the theoretical maximum surface coverage, which is calculated based on the molecular size derived from the bond lengths, angles, and atom sizes of fluorocarbon.

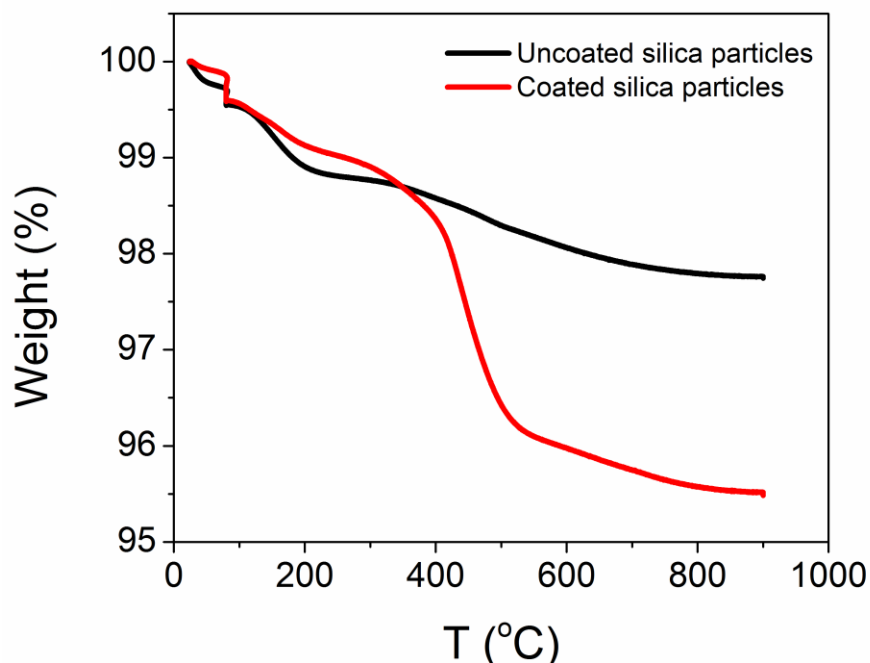


Figure 4.5: TGA curves for uncoated and coated particles, showing a weight loss of 2.3 wt% and 4.5 wt% for uncoated and coated particles when temperature increases to ~900 °C, respectively.

4.3.2 Particle Size

4.3.2.1 Scanning Electron Microscopy (SEM)

The dried silica particles before and after surface coating are recorded by SEM and the particle size distribution is analyzed by ImageJ software.¹ For example, Figure 4.6A is the raw SEM image and this SEM image is analyzed by software ImageJ to calculate the number-averaged nanoparticle radius as shown in Figure 4.6B. Particles of blue color in the image are accounted in the statistical analysis while particles of black color are excluded due to overlapping issues. Area distribution of the blue-color particles is shown in Figure 4.6C, representative of a Gaussian

distribution function. The number-average radius and standard deviation of the uncoated particles are then calculated to be 45.3 ± 5.3 nm, which is in a good agreement with manufacturer.

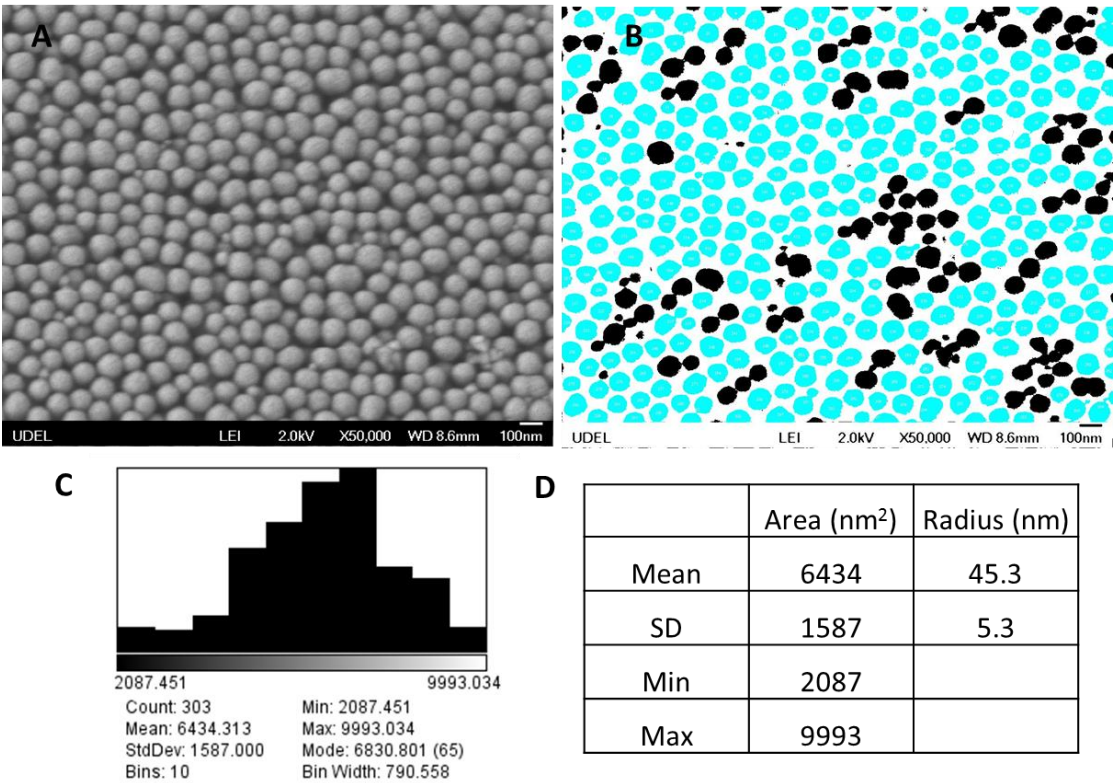


Figure 4.6: Particle size analysis of dried, uncoated silica particles. (A) Raw SEM image; (B) SEM image processed by ImageJ software: blue indicates the particles are considered in the area distribution analysis; black indicates the particles are excluded from the analysis (C) Histogram of particle area distribution; (D) Statistical results of the area and radius of the silica particles.

After coating, the size distribution of the coated silica particle is evaluated using the same method as for uncoated particle and is shown in Figure 4.7. The

number-averaged particle size and standard deviation for coated particles are 53.6 ± 10.0 nm, which are slightly larger than for the uncoated silica particles. This larger average particle size could result from the surface coating as well as lower statistical accuracy. In Figure 4.7B, fewer single particles (blue-color) are considered in the statistical analysis as most of the particles are overlapped with each other in this SEM image analysis. Due to the limited particle population studied using SEM image analysis, other independent analytical methods involving great particle population, such as DLS and SANS measurements, are employed to characterize the particle size distribution.

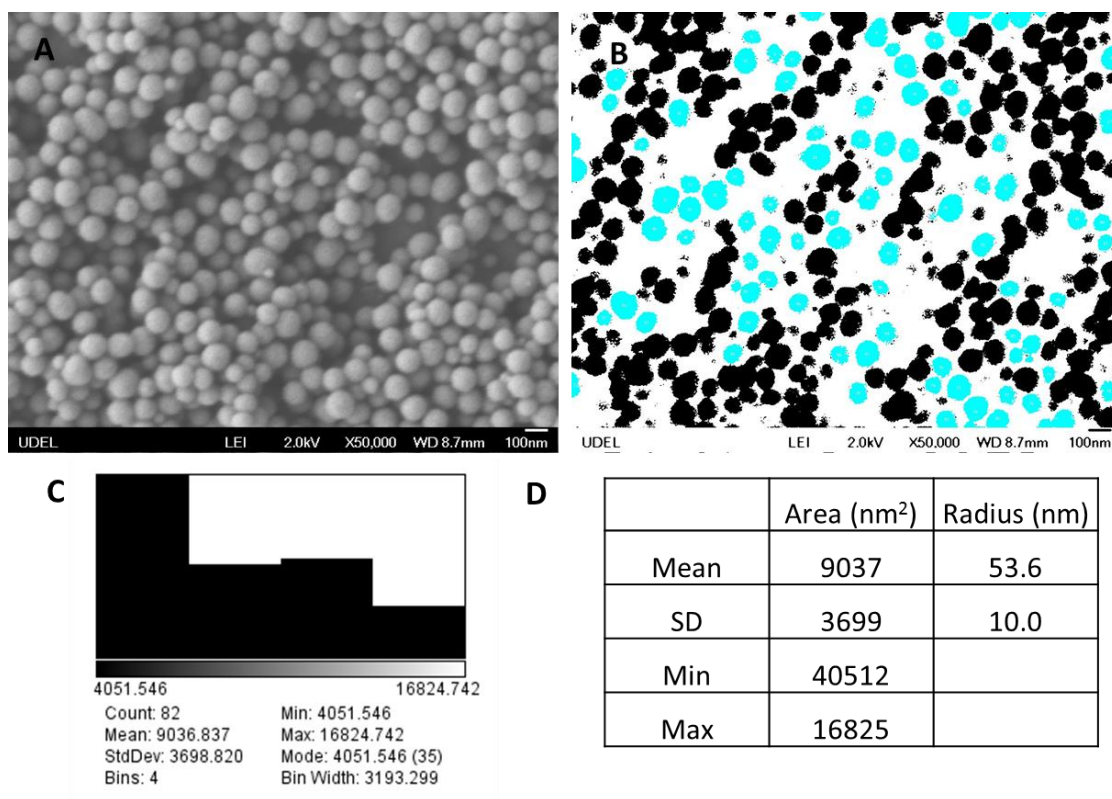


Figure 4.7: Particle size analysis of dried, coated silica particles. (A) Raw SEM image; (B) SEM image analyzed by ImageJ software: blue indicates the particles are considered in the area distribution analysis; black indicates the particles are excluded from the analysis (C) Histogram of particle area distribution; (D) Statistical results of the area and radius of the silica particles.

4.3.2.2 Dynamic Light Scattering (DLS)

The size distributions of uncoated and coated particles in various polar solvents and in $[C_4mim][BF_4]$ were measured by DLS and are shown in Figure 4.8. Uncoated silica particles are well dispersed in H_2O and fluorocarbon coated silica particles are well dispersed in ethanol with a narrow size distribution. The shape of the size distribution of the coated silica particles is similar to that for the uncoated particles with a slight shift to larger sizes, which likely is due to the addition of surface coating.

It is evident that the uncoated silica particles aggregate in ionic liquid [C₄mim][BF₄] even after sonication and extensive mixing, exhibiting a broader size distribution and a much larger averaged particle size. In contrast, the coated particles disperse in [C₄mim][BF₄] as evinced by a much narrower size distribution.

The values of the number-averaged particle size from the DLS measurements are listed in Table 4.2. The results of coated particles in ethanol demonstrate that the addition of the fluorocarbon coating increases the radius of particles by an amount consistent with the molecular size of the fluorocarbon (~ 14 Å), as estimated from the bond lengths and angles. However, there is an anomalous increase in hydrodynamic radius observed for the particles dispersed in the ionic liquid, which is the consequence of solvation layers forming near the particle surface. This solvation layering will be discussed in details in Chapter 5.

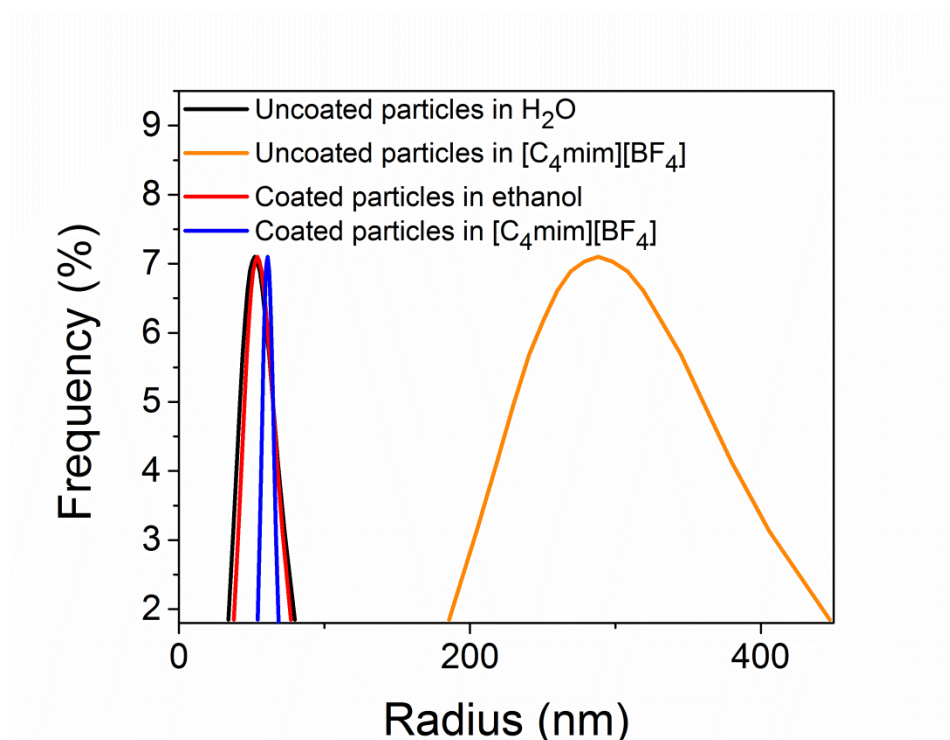


Figure 4.8: Size distribution of uncoated and coated particles suspended in various solvents from DLS measurement.

Table 4.2: Particle radii for uncoated and coated particles in various solvent measured by DLS.

Solutions	Uncoated particle in H ₂ O	Uncoated particle in [C ₄ mim][BF ₄]	Coated particle in ethanol	Coated particle in [C ₄ mim][BF ₄]
Radius (nm)	53.8 ± 4.8	298.6 ± 28.1	55.2 ± 3.8	60.4 ± 3.0

4.3.2.3 Small-Angle Neutron Scattering (SANS)

SANS measurements of dilute nanoparticle suspensions are performed to further quantify the particle size, polydispersity, and coating layer structure. The measured SANS intensities for dilute dispersions ($\phi = 0.004$) of uncoated and coated particles in different solvents at 25 °C are shown in Figure 4.9. The general shapes of

the scattering spectra are similar as expected, given that the particles have the same core, which dominates the scattering intensity. The differences in scattering intensities reflect the differences in the neutron scattering length densities of the solvents, which is also evident in the different background intensities observed at high values of scattering vector q . The scattering intensity from the dispersion of uncoated particles in H₂O is fitted by varying particle size, polydispersity, and volume fraction with a Schulz-distributed sphere model⁴ using the known scattering length densities (SLD) for the core and solvent. The measured scattering intensities from dispersions of coated particles in ethanol and [C₄mim][BF₄] are fitted by a core-shell model and varying the shell thickness, volume fraction, and scattering length density of the shell under constraints. The fitting parameters are summarized in Table 4.3. In the fitting, the volume fraction of the dispersion is restricted with the particle concentration calculated from mass with uncertainty, the shell thickness is constrained by the extended molecular size of fluorocarbon, and the scattering length density of the shell is constrained within the range of the SLD of solvent and fluorocarbon. From the fits, I extract individual particle properties such as core size, polydispersity, and coating thickness. As the density of ionic liquid solvation layers is close to the bulk ionic liquid, there is no significant scattering length density difference between the solvation layers and the ionic liquid. Therefore, the solvation layers are not detected directly by neutron scattering. Note that the shell SLD determined from the fit is close to the value calculated for the pure fluorocarbon. This suggests that the large molecular size of fluorine in the fluorocarbon chains (fluorocarbon chains occupy 60 vol% of the shell) prevents significant solvent penetration into the coating. Analysis of the SANS form factor measurements, summarized in Table 4.4, yield a particle radius of $54.2 \pm$

5.4 nm for the core particles with 10.5% polydispersity (p) and shell thickness of 0.9 nm and 1.2 nm for particles dispersed in ethanol and $[\text{C}_4\text{mim}][\text{BF}_4]$, respectively. These measurements further confirm the presence of the fluorocarbon coating and show that the fluorocarbon brush is more extended in $[\text{C}_4\text{mim}][\text{BF}_4]$, which suggests a better compatibility with $[\text{C}_4\text{mim}][\text{BF}_4]$ than with ethanol.

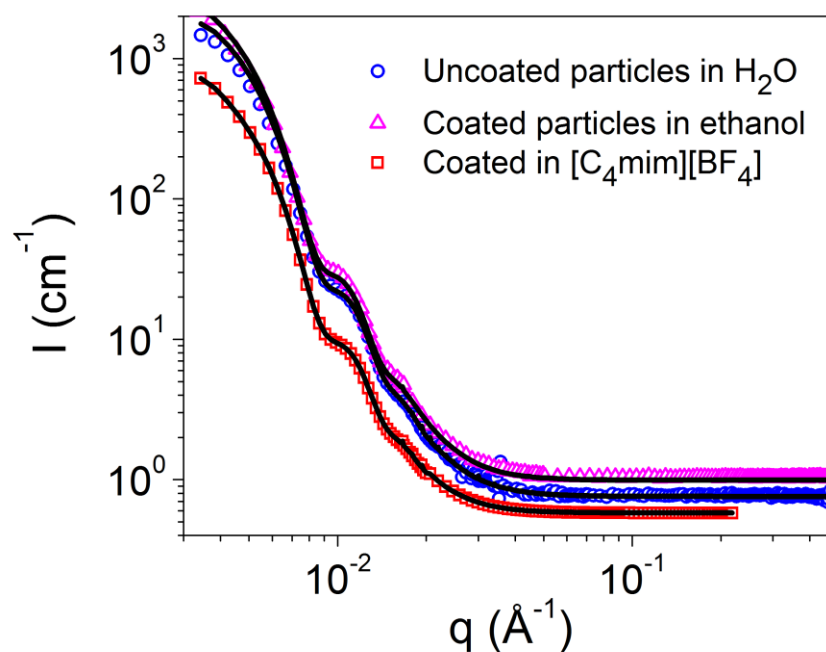


Figure 4.9: Measured SANS scattering intensity at 25 °C for three dilute dispersions and corresponding fits: uncoated particles in H_2O , coated particles in ethanol and in ionic liquid $[\text{C}_4\text{mim}][\text{BF}_4]$, respectively.

Table 4.3: The parameters used for SANS form factor fittings.

Parameters	Uncoated particles in H ₂ O	Coated particles in ethanol	Coated particles in [C ₄ mim][BF ₄]
ϕ	0.0036 ^b	0.0048 ^b	0.0032 ^b
$\bar{r}$ (nm)	54.2 ^b	54.2 ^a	54.2 ^a
p	0.105 ^b	0.105 ^a	0.105 ^a
δ (shell, nm)	...	0.9 ^b	1.2 ^b
SLD _{core} (A ⁻²)	3.47×10^{-6} ^a	3.47×10^{-6} ^a	3.47×10^{-6} ^a
SLD _{shell} (A ⁻²)	...	3.24×10^{-6} ^b	3.24×10^{-6} ^b
SLD _{solvent} (A ⁻²)	-5.60×10^{-6} ^a	-3.45×10^{-7} ^a	1.40×10^{-6} ^a
Background (cm ⁻¹)	0.76 ^a	0.99 ^a	0.62 ^a

a- The parameters are fixed as constant.

b- The parameters are fitted under constraints.

The average radii of the uncoated and coated particles obtained from DLS and SANS are summarized and compared in Table 4.4. An estimate of the solvation layer of ~ 5 nm can be made by comparing the difference between the hydrodynamic radius in [C₄mim][BF₄] measured by DLS and the core-shell radius determined by SANS measurements. A solvation layer is not detected by SANS fits to the form factor, but it will increase the particle radius and thus, slow the diffusion and yield an apparently larger particle size in DLS. More detailed analysis of solvation layers can be found in Chapter 5.

Table 4.4: Summary of particle radii for uncoated and coated particles with various methods.

Measurement Techniques	Uncoated particle in H ₂ O	Coated particle in ethanol	Coated particle in [C ₄ mim][BF ₄]
DLS	53.8 ± 4.8 nm	55.2 ± 3.8 nm	60.4 ± 3.0 nm
SANS	54.2 ± 5.4 nm $p = 10.5$ %	Core: 54.2 ± 5.4 nm $p = 10.5$ %	Core: 54.2 ± 5.4 nm $p = 10.5$ %
Brush	...	0.9 nm	1.2 nm

4.3.3 Particle Density

To calculate the accurate volume fraction of particles in dispersion, it is crucial to obtain an accurate particle density. The densities of both uncoated and coated silica particles are obtained through gravimetric densitometry using equation 4-1. Densitometry was performed on the uncoated particles suspended in 0.1 mM NaCl/H₂O (pH = 9.1 ± 0.1) solution, and the coated particles suspended in [C₄mim][BF₄] at 25 °C using an Anton Paar DMA-4500M densitometer. The experimental results can be found in Figure 4.10. The skeletal particle density in solution is extracted from a linear regression of equation 4-1 to the data and found to be $\rho = 2.210 \pm 0.005 \text{ g/cm}^3$ and $\rho = 2.167 \pm 0.007 \text{ g/cm}^3$ for the uncoated and coated particles, respectively. The reduction in solution density of the coated particles is attributed to the contribution from the surface layer, where the fluorocarbon coating is expected to have a lower density than the silica nanoparticle.

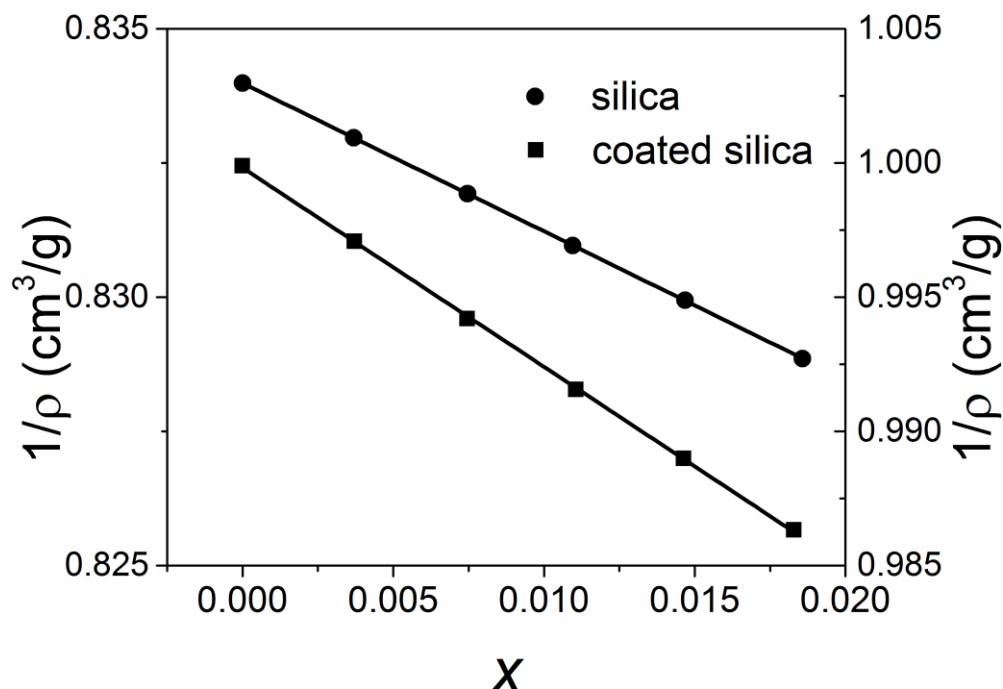


Figure 4.10: Results of the densitometry experiments for the uncoated silica particles in mother liquid (secondary y axis, right) and fluorocarbon coated silica particles in $[C_4mim][BF_4]$ (primary y axis, left). The lines represent a fit of equation 4-1 to the inverse of the suspension density and the mass fraction of the disperse phase.

4.4 Conclusions

Fluorocarbon 1H,1H,9H hexadecafluoro-1-nonanol coated silica particles are synthesized through dehydration reaction following the procedure of van Helden *et al.* The surface coating is confirmed by 1H NMR and the grafting density is measured by TGA determined to be 1.4 chain/nm² with 60 % surface coverage. The particle size distributions of uncoated and coated silica particles are measured by independent techniques, such as SEM, DLS, and SANS measurements, resulted consistent agreement with each other, indicating the size of the particles is on the order of ~ 100

nm with 10% polydispersity. The thickness of coated brush is determined to be ~ 1 nm, which is consistent with the molecular size of the fluorocarbon (~ 1.4 nm) as estimated from the bond lengths and angles. The coated silica particles disperse well in the ionic liquid $[\text{C}_4\text{mim}][\text{BF}_4]$ due to the formation of solvation layers, which will be discussed in detail in Chapter 5, while, uncoated particles aggregate in the same ionic liquid. The skeletal particle densities of uncoated and coated silica particles are measured by densitometry and are used to convert the particle mass fraction loading to volume fraction in this dissertation.

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Chapter 5

FLUOROCARBON COATED PARTICLE SYSTEM – STABILIZATION MECHANISM AND INTERFACIAL STRUCTURE

In this chapter, stable solid silica nanoparticle dispersion in ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate [C₄mim][BF₄] is achieved and the stabilization mechanism of silica particle in ionic liquid is investigated. The critical role of solvation forces in dispersing and stabilizing nanoparticles and colloids in [C₄mim][BF₄] is demonstrated. Stable silica nanoparticle suspensions over 60 wt% solids are obtained by particle surface chemical functionalization with a fluorinated alcohol. A combination of techniques including rheology, dynamic light scattering (DLS), transmission electron microscopy (TEM), and small angle neutron scattering (SANS) are employed to determine the mechanism of colloidal stability. Solvation layers of ~ 5 nm at room temperature are measured by multiple techniques, and are thought to be initiated by hydrogen bonds between the anion [BF₄]⁻ and the fluorinated group on the surface coating. Inducing structured solvation layering at particle surfaces through hydrogen bonding is demonstrated as a method to stabilize particles in ionic liquids. Text and figures are reproduced and adapted with permission from Gao J., et al. *ACS Nano* 2015, 9, (3), 3243-3253.

5.1 Introduction

Many applications of ionic liquids require successfully dispersing nanoparticles across a broad range of conditions. Studies of colloidal systems in ionic liquids include nanoparticle synthesis,¹⁻² phase transfer,³ catalytic reactions medium as

a “green” solvent,⁴⁻⁵ the self-assembly of surfactants,⁶⁻⁷ and block copolymer mesophases.⁸⁻⁹ However, there are relatively few studies of the stability of colloidal particles in ionic liquids and these have been primary empirical,¹⁰⁻¹⁷ despite the fact that nanoparticle stability is of critical importance in determining the suspension rheology and controlling aggregation, gel and glass formation, as well as in the performance of ionic liquid based lubricants. It is apparent from the limited reports in the literature that particle dispersion and stability in ionic liquids depends on the specific chemical composition of the ionic liquid as well as the surface chemistry of the particles.^{12, 16-17}

The shear viscosity of hydrophilic and hydrophobic fumed silica colloidal dispersions in various ionic liquids were measured, in which shear thinning, shear thickening, and gelation were reported.¹² The effect of particle size and surface hydrophobicity of fumed silica particle on particle stability and suspension properties in [C₄mim][BF₄] have been investigated and can be found in Appendix B. An increase of the alkyl chain length of the cation has been reported as beneficial for stabilizing TiO₂ nanopowders in 1-alkyl-3-methylimidazolium tetrafluoroborate ([C_nmim][BF₄]) ionic liquids.¹⁷ Spherical silica nanoparticles were reported to aggregate in imidazolium-based ionic liquids by Ueno *et al.*,¹⁰ while grafting polymer such as poly(methyl methacrylate) (PMMA) to the particle surface improved suspension stability in ionic liquids.^{10, 13} For example, PMMA-grafted silica nanoparticles show good dispersion in 1-butyl-3-methylimidazolium hexafluorophosphate ([C₄mim][PF₆]) and 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C_nmim][NTf₂]), presumably because PMMA is itself soluble in these solvents; however, such coated particles show poor dispersion if

PMMA is insoluble in the ionic liquids (*e.g.*, [C₄mim][BF₄]).¹⁰ Here the mechanism of stability is afforded by the steric repulsion between the grafted layers of significant extent and as is typical with such systems, the system will become unstable when the brush is immersed into a poor solvent and collapses.¹⁸

Particle stability in dispersions is typically treated within the classical framework of colloid science, namely the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory, which accounts for van der Waals attraction and electrostatic repulsion between particles in solution.¹⁹ Due to the ionic nature of the solvent, electrostatic stabilization is not sufficient to stabilize particles in ionic liquids against the ubiquitous attraction from dispersion forces between the particles.¹⁰ The high ionic strength in ionic liquids effectively screens the electrostatic repulsion between silica particles. The screening of the electrical potential and electrical double layers at charged solid surfaces in ionic liquids and molten salts²⁰ has been investigated by experiments²¹ and simulations.²²⁻²³ The electrical double layer in ionic liquid [C₄mim][BF₄] has been determined to be one-ion thick layer (about 4 Å thickness) using sum frequency generation vibrational spectroscopy (SFG), electrochemical impedance spectroscopy (EIS), and the vibrational Stark effect.²¹

Due to this screening effect, surface-adsorbed or grafted surfactants and polymers, which are soluble in the ionic liquid, are introduced to provide stability.¹⁸ However, there are rare cases where “bare” particles disperse into ionic liquids, *e.g.*, hydrophilic fumed silica particles can be dispersed into an aprotic ionic liquid, [C₄mim][BF₄] in the absence of any stabilizer.^{12, 14, 24} This unexpected stability is hypothesized to be induced by solvation forces arising from solvent structuring near the particle surfaces, and the fact that the particles are often porous aggregates such

that van der Waals attractions are weak.^{13-14, 24} There is evidence for such solvation forces occurring at macroscopic surfaces: Oscillating solvation forces have been observed between macroscopic mica and silica surfaces in both protic and aprotic ionic liquids as detected by surface force measurements,²⁵⁻³⁰ and these observations have been qualitatively reproduced by molecular dynamics simulation.³¹ These measurements and simulations indicate that the ion pairs are arranged in a layered structure near the solid surfaces.²⁹ Other evidence supporting the existence of solvation layers in particle dispersions include the increase in fumed silica particle stability in [C₄mim][BF₄] upon addition of lithium salt which is presumed to stabilize the solvation layers.²⁴ Furthermore, silica particle suspensions lose stability in the presence of small amounts of water, which decreases the structuring of solvation layers.^{14, 32} However, to date, there are no direct measurements of the solvation-induced structuring in ionic liquids around nanoparticle surfaces or a predictive, quantitative knowledge of inter-particle interactions in ionic liquids that can be used to predict and control colloidal stability.

To directly test this hypothesis and to develop a strategy for dispersing nanoparticles in ionic liquids more generally, I study the nanostructure, stability, and dynamics of model spherical silica particles surface-functionalized in a common aprotic ionic liquid [C₄mim][BF₄]. Surface modification using a small fluorocarbon molecule 1H,1H,9H hexadecafluoro-1-nonanol induces solvation layering around silica particles, leading to dispersion stability. The choice of this surface modifier is motivated by the research of Shiflett and Yokozeki,³³ who studied the behavior of fluorocarbons in room temperature ionic liquids and found a wide range of solubility that correlated with hydrogen bonding. I propose that hydrogen bonding between the

fluorinated anion in the ionic liquid $[\text{C}_4\text{mim}][\text{BF}_4]$ and the terminal hydrogen group on the surface coating drives the formation of solvation layers that impart colloidal stability by steric repulsion. Figure 5.1 shows a schematic representation of such solvation layers, based on the dimensions determined in this work. Note that my methods cannot determine the molecular orientation in the layers and the molecular details in the schematic are based on related literature work.²⁹⁻³⁰ This study presents the first direct measurements of the extent of the formation of these solvation layers around nanoparticles in ionic liquid $[\text{C}_4\text{mim}][\text{BF}_4]$ using TEM, rheology, DLS, and SANS.

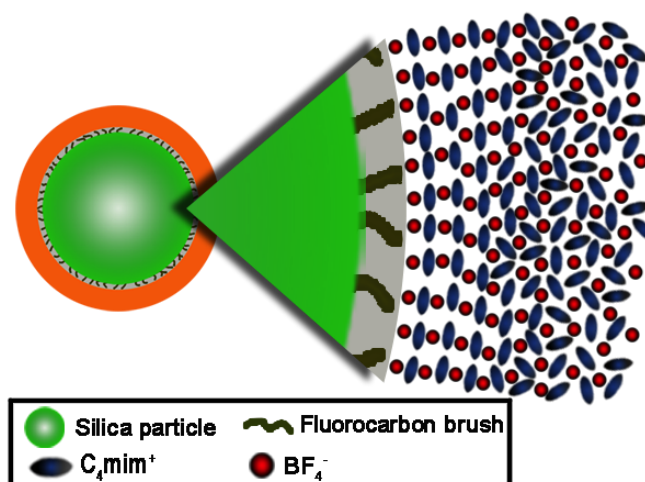


Figure 5.1: Schematic illustration of a coated silica nanoparticle stabilized by solvation layers in ionic liquid $[\text{C}_4\text{mim}][\text{BF}_4]$. Note the ion structure in the layers is schematic.

5.2 Materials and Methods

5.2.1 Particle Suspension Preparation

The ionic liquid $[\text{C}_4\text{mim}][\text{BF}_4]$ (>99% pure, Iolitec, Figure 5.2B), was dehydrated under vacuum condition at 70 °C for 24 h prior to use. The final water content was 373 ppm as determined by the Karl Fischer titration. Fluorocarbon 1H,1H,9H hexadecafluoro-1-nonanol (Figure 5.2A) coated silica particles are synthesized and stored following the protocol described in Chapter 4.

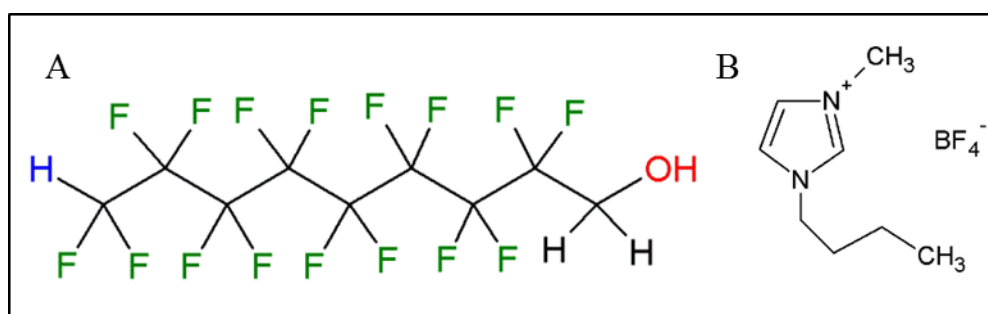


Figure 5.2: Chemical structure of fluorocarbon 1H,1H,9H hexadecafluoro-1-nonanol used to functionalize the particle surface (A) and ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ($[\text{C}_4\text{mim}][\text{BF}_4]$) (B).

Dispersions of coated particles were prepared by first drying the fluorocarbon-coated silica under a nitrogen stream and then under vacuum for 24 h. The particles were dispersed in dehydrated ionic liquid at varying concentrations from dilute through concentrated. For the uncoated silica particle dispersions, the particles were thoroughly washed 3 times with water using a Sorvall RC6+ centrifuge to remove the sodium stabilizer before sample preparation. All the dispersions were mixed using a vortex mixer (3 min at 3000 RPM), sonication water bath (4 h at room temperature)

and roll mixer (72 h at room temperature) to ensure homogeneity, followed by a 5 min degassing to remove air bubbles in the samples. As the presence of water decreases the structure of solvation layer and reduce the particle stability,^{32, 34} the samples were dehydrated again in a vacuum oven at 70 °C for 24 h prior to each measurement and the water content was 1194 ppm as measured by the Karl Fischer titration. All of the dispersion samples were prepared by weight and converted to volume fraction using the measured particle and solvent densities in Table 5.1. The coated particles in [C₄mim][BF₄] dispersion samples are stable at room temperature and no sedimentation is observed after 6 months.

Table 5.1: Densities of particles, fluorocarbon and solvents at 25 °C.

	silica	coated silica	fluorocarbon	[C ₄ mim][BF ₄]	H ₂ O	ethanol
ρ (g/cm ³)	2.210 ± 0.005	2.167 ± 0.007	1.646*	1.201 ± 0.001	0.997 ± 0.001	0.789*

* The densities of fluorocarbon and ethanol are from material safety data sheet. All the others are measured or calculated from densitometry as discussed in Chapter 4.

5.2.2 Derjaguin-Landau-Verwey-Overbeek (DLVO) Inter-particle Potential Calculation

According to the DLVO theory, the total interparticle potential $\Phi_{total}(d)$ can be written as the sum of an attractive London-van der Waals potential $\Phi_{vdw}(d)$ and a repulsive electrostatic potential $\Phi_{vdw}(d)$ due to the charge of the particles¹⁹

$$\Phi_{total}(d) = \Phi_{vdw}(d) + \Phi_{ele}(d), \quad 5-1$$

where d is the distance between the particle surfaces. $\Phi_{vdw}(d)$ between two identical spherical silica particles of radius r is given by³⁵

$$\Phi_{vdw} = -\frac{1}{6}A \left(\frac{2r^2}{a^2 - 4r^2} + \frac{2r^2}{a^2} + \ln \frac{a^2 - 4r^2}{a^2} \right), \quad 5-2$$

where a is the two particles center-center separation, $a = 2r + d$. A is the Hamaker constant (two silica dioxide phases interacting across solvent) and can be calculated from the relative dielectric constant ε and refractive index n of silica dioxide and solvent based on the Lifshitz theory

$$A = \frac{3}{4}k_B T \left(\frac{\varepsilon_p - \varepsilon_s}{\varepsilon_p + \varepsilon_s} \right)^2 + \frac{3h\nu_e}{16\sqrt{2}} \frac{(n_p^2 - n_s^2)^2}{(n_p^2 + n_s^2)^{3/2}}, \quad 5-3$$

where k_B is the Boltzmann constant, T is the absolute temperature, h is Planck's constant, which is 6.63×10^{-34} J·s, and ν_e is the frequency of the main electronic absorption for the dielectric permittivity, which can be taken to be 3×10^{15} s⁻¹ for water and [C₄mim][BF₄]. The Hamaker constant of silica particles in mother liquid is assumed to be identical as for that in H₂O.

The repulsive electrostatic potential $\Phi_{vdw}(d)$ of spheres with thin double-layers in ionic liquids and with constant potential in H₂O are given respectively by³⁶

$$\Phi_{ele} = 32\pi r \varepsilon_s \varepsilon_0 \left(\frac{k_B T}{ze} \right)^2 \tanh^2 \left(\frac{\psi_s ez}{4k_B T} \right) \exp(-\kappa d), \quad 5-4$$

$$\Phi_{ele} = 2\pi r \varepsilon_s \varepsilon_0 \left(\frac{k_B T}{ze} \right)^2 \left(\frac{\psi_s ez}{k_B T} \right)^2 \ln(1 + e^{-\kappa d}), \quad 5-5$$

where ε_s is the relative dielectric permittivity of solvent, ε_0 is dielectric constant, which is 8.85×10^{-12} C² / (J·m), z is the symmetric electrolyte of valence, e is unit charge 1.60×10^{-19} C, ψ_s is the surface potential, and κ is the Debye reciprocal length parameter. Debye length κ^{-1} is calculated as follows³⁵

$$\kappa^{-1} = \sqrt{\frac{\varepsilon_s \varepsilon_0 k_B T}{1000 e^2 N_A \left(\sum_i z_i^2 M_i \right)}}, \quad 5-6$$

where z_i is the electrolyte valence of solvent, M_i is the molar concentration of electrolyte, and N_A is the Avogadro's number, which is $6.02 \times 10^{23} \text{ mol}^{-1}$.

The Zeta potential is used as an estimation of nanoparticle surface potential for the electrostatic force calculation. Because of the high ionic strength and non-aqueous feature of ionic liquid [C₄mim][BF₄], it was difficult to measure the zeta potential with a conventional electrokinetic method in the ionic liquid colloid system.¹⁰ The zeta potential of silica particles in [C₄mim][BF₄] is calculated by assuming the charge density of silica nanoparticles in [C₄mim][BF₄] is the same as that measured in the sodium chloride (NaCl) aqueous solution of 1.25M concentration. The Debye length in ionic liquid [C₄mim][BF₄] is estimated from electrical double layer measurement using sum frequency generation vibrational spectroscopy (SFG), electrochemical impedance spectroscopy (EIS).³⁷ Uncoated silica particles are dispersed in aqueous solution (0.1 mM (pH = 9.1 ± 0.1) NaCl solution: mother liquid) to measure the zeta potential of silica nanoparticles in the aqueous solution using a Brookhaven ZetaPals instrument.

5.2.3 Characterization Techniques

TEM images of the nanoparticles were recorded using a JEOL JEM-2000FX (LaB6) TEM operated at 200 kV in the Keck Microscope facility at the University of Delaware. The dried, coated particles were imaged after the ethanol of coated particle/ethanol solution drops dried on the carbon-sputtered copper grid. The coated particles dispersed in [C₄mim][BF₄] were imaged directly in their solution phase. Samples were prepared by placing a small droplet of dilute coated

particle/[C₄mim][BF₄] dispersion onto a carbon-sputtered copper grid and extra solution was removed by blotting with filter paper, leaving a thin film of dispersion on the grid.

Rheological measurements were performed on a TA Instruments AR-G2 stress controlled rheometer at 25 °C with Peltier plate temperature control, and a 40 mm stainless steel cone with 2° cone angle with solvent trap. Conversion between applied and measured parameters (torque M and strain γ) and the rheological material functions were performed using the TA Instruments Trios software. To erase any previous shear histories and maintain a consistency between measurements, a steady pre-shear was applied at a shear stress of 10 Pa for 2 min before each dynamic rheological measurement. A steady state shear measurement is performed as a function of shear stress for two different concentrations (volume fraction = 0.2 and 0.3) suspensions. For the steady shear tests, the viscosity responses are reversible. An ascending and descending shear stress loop was performed, and there is no observed hysteresis or thixotropic effects during steady shear. Each measurement was repeated three times for accuracy.

SANS measurements were performed at the National Institute of Standards and Technology (NIST) Center for Neutron Research (NCNR) in Gaithersburg, MD on both NG3 and NG7 beamlines. Samples were loaded into demountable titanium cells with a 1 mm path length. The cell temperatures were maintained to ± 0.1 °C using the 10 CB, 10 position sample cell holder with fluid bath. A wide range in scattering wavevector q was obtained by combining scattering intensity from four different instrument configurations at detector distances of 1, 4, 13, and 15.3 m with lens. The wavelength for 1, 4, and 13 m configurations is 6.0 Å and 8.0 Å for 15.3 m with lens.

The SANS scattering intensity profiles were reduced to absolute scale and analyzed using the standard protocol discussed in Chapter 2.

SANS spectra are analyzed following the protocol in Chapter 2. The scattering length density (SLD) of particles and solvents were calculated using measured densities (Table 5.1) by NIST NCNR online tools: Neutron activation and scattering calculator.³⁸ Properties of the dispersions were determined by modeling the measured SANS intensity using a form factor model for polydisperse core-shell particles (Core-shell with Schultz distributed core) and a monodisperse structure factor model that includes hard core repulsion with contact attraction (Sticky hard sphere model). The SANS spectra of particle solutions are described by the function

$$I(q) = n_p \bar{P}(q, \rho_{i(SLD)}, \phi, \bar{r}, p, \delta) S(q, \phi_{eff}, \bar{r}_{eff}, \tau, \varepsilon) + bkg, \quad 5-7$$

where n_p is the particle number density, $n_p = \phi / \langle V \rangle$, $\langle V \rangle$ is the average of single particle volume, and bkg is the background level. $\bar{P}(q, \rho_i, \phi, \bar{r}, p, \delta)$ is the form factor, which describes the scattering from individual particles, and is a function of wavevector q , particle, solvent, and shell scattering length density $\rho_{i(SLD)}$, particle volume fraction ϕ , core particle average size $\bar{r}$, polydispersity p , and shell thickness δ . $S(q, \phi_{eff}, \bar{r}_{eff}, \tau, \varepsilon)$ is the structure factor, which contains information of interparticle interactions and spatial arrangement of particles; and it is a function of wavevector q , effective particle volume fraction ϕ_{eff} , effective particle average size $\bar{r}_{eff}$, interaction parameter τ (Baxter temperature) and ε (Perturbation parameter). The structure factor is calculated using the Ornstein–Zernike³⁹ (OZ) equation with the Percus–Yevick⁴⁰ (PY) closure approximation scaled by the mean effective particle diameter. For dilute dispersions, the interactions between particles can be ignored and the structure factor $S(q, \phi_{eff}, \bar{r}_{eff}, \tau, \varepsilon) \sim 1$.

The expression for the core-shell form factor with Schultz distributed core and constant shell is

$$\bar{P}(q, \rho_i, \phi, \bar{r}, p, \delta) = \int_0^{\infty} f(R, \bar{r}, p) \left[(\rho_{shell} - \rho_{solvent}) F(q, R + \delta) + (\rho_{core} - \rho_{shell}) F(q, R) \right]^2 dR \quad 5-8$$

where $f(R)$ is the Schultz distribution function. The interference factor $F(q, R)$ is that for a spherical object in the Rayleigh–Gans–Debye limit:⁴¹

$$F(q, R) = 3V_p \frac{\sin(qR) - qR \cos(qR)}{(qR)^3}. \quad 5-9$$

5.3 Results and Discussion

5.3.1 Dilute Particle Dispersions – Single Particle Properties

The silica nanoparticles as supplied are dispersed in water, but will aggregate if they are dispersed into [C₄mim][BF₄]. This is in direct contrast to the surface functionalized nanoparticles - fluorocarbon-coated nanoparticles, which readily disperse and remain stable in [C₄mim][BF₄] but do not disperse in water. TEM images comparing the dried fluorocarbon-coated silica particles and fluorocarbon-coated silica nanoparticles dispersed in [C₄mim][BF₄] are shown in Figure 5.3. The synthesis procedure for coating the fluorocarbon to the surface of the silica nanoparticle as discussed in Chapter 2 has no effect on the silica nanoparticle core shape or size. Figure 5.3B shows the dispersion of the particles by direct observation using *in situ* TEM, which is possible in the ionic liquid medium despite the high vacuum condition and electron beam irradiation of electron microscope chamber.² The lower resolution for the image in the ionic liquid is due in part to the Brownian

motion of the particles and possible flow of the dispersion on the grid during the imaging.

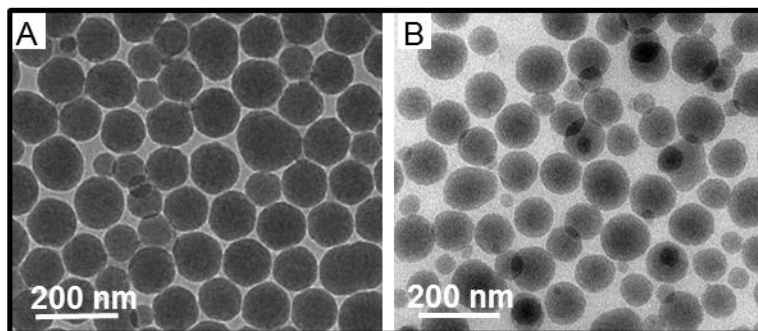


Figure 5.3: Transmission electron microscopy (TEM) images of (A) the dried fluorocarbon-coated particle and (B) fluorocarbon-coated particles in $[C_4mim][BF_4]$.

The hydrodynamic radii of uncoated and coated silica nanoparticles in polar solvents (e.g., water, ethanol) and the ionic liquid are measured by dynamic light scattering (see Chapter 4 Section 4.3.2.2). The results in ethanol demonstrate that addition of the fluorocarbon coating increases the radius of particles (Table 5.2) by an amount consistent with the molecular size of the fluorocarbon (~ 1.4 nm) as calculated from the bond lengths and angles. However, there is an anomalous increase in hydrodynamic radius observed for the particles dispersed in the ionic liquid. Detailed analysis of the size distributions in Chapter 4 Section 4.3.2.2, coupled with the direct TEM observations, show that this increase in hydrodynamic size is not due to a small amount of aggregation, but rather, is the consequence of solvation layers forming near the particle surface that increase the hydrodynamic size of the particles. Note that the uncoated silica particles will not disperse in $[C_4mim][BF_4]$ even after sonication and

extensive mixing; DLS measurements on these systems yield a broader size distribution and a much larger particle size indicative of aggregation as discussed in Chapter 4 Section 4.3.2.2.

Table 5.2: Summary of particle hydrodynamic radii for uncoated and coated particles in different solvents measured by various technique methods.

Measurement Techniques	Uncoated particle in H ₂ O	Coated particle in ethanol	Coated particle in [C ₄ mim][BF ₄]
DLS	53.8 ± 4.8 nm	55.2 ± 3.8 nm	60.4 ± 3.0 nm
SANS	54.2 ± 5.4 nm <i>p</i> = 10.5 %	Core: 54.2 ± 5.4 nm <i>p</i> = 10.5 %	Core: 54.2 ± 5.4 nm <i>p</i> = 10.5 %
Brush	...	0.9 nm	1.2 nm
Schematic illustration			

5.3.2 DLVO Potential between Two Silica Particles

The interaction potentials between two silica particles in solution can be calculated from the DLVO theory. The parameters used to calculate the van der Waals, electrostatic, and DLVO potentials are listed in Table 5.3. The DLVO potential profiles of two uncoated silica nanoparticles (*R* = 54.2 nm) in [C₄mim][BF₄] and mother liquid at 25 °C are shown in Figure 5.4 as a function of the surface separation distance *d*. The DLVO potential for silica nanoparticles in the aqueous mother liquid is positive for *d* > 0.1 nm (Figure 5.4B), indicating long-range repulsion leading to particle stabilized by electrostatic forces, in agreement with observation.

However, for silica nanoparticles dispersed in $[\text{C}_4\text{mim}][\text{BF}_4]$ as shown in Figure 5.4A, the electrostatic repulsion is screened and the DLVO potential is negative, indicating the particles are attracted to each other at all separation distances. Thus, the DLVO calculations predict that the uncoated silica particles can be electrostatically stabilized in mother liquid, but not in $[\text{C}_4\text{mim}][\text{BF}_4]$, which agrees with experimental results.

The addition of the fluorocarbon coating will provide a steric barrier to keep particles apart. However, the calculations in Figure 5.4A show that the particles with the fluorocarbon will still have a weak attraction $O(k_B T)$ sufficient to induce weak flocculation if the coating acts as a ~ 1 nm steric layer keeping particle surfaces ~ 2 nm apart. However, DLS measurements show that the silica nanoparticles are surrounded by ~ 5 nm solvation layers such that minimum separations of $d \approx 10$ nm are anticipated. At this separation distance, the DLVO attractive potential between nanoparticles is negligible (Figure 5.4A), confirming that these coated nanoparticles can be stabilized by inducing the formation of solvation layers in $[\text{C}_4\text{mim}][\text{BF}_4]$.

Table 5.3: Parameters for the calculation of the DLVO potential for colloidal dispersions in $[\text{C}_4\text{mim}][\text{BF}_4]$ and H_2O /mother liquid at 25 °C.

Materials	ε	n	A (10^{-21}J)	ψ_s (mV)	M (mol/L)	κ^{-1} (nm)
Silica	4.42	1.46	---	---	---	---
$[\text{C}_4\text{mim}][\text{BF}_4]$	11.70	1.42	1.04	-9.48	---	0.4
H_2O / mother liquid	78.54	1.33	6.97	-36.57	1×10^{-4}	30.5

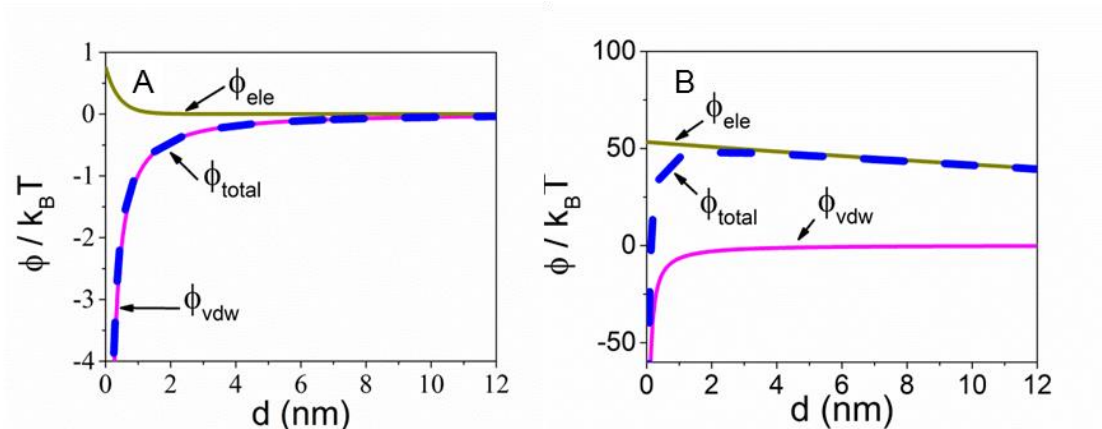


Figure 5.4: Calculated DLVO interparticle potential profiles at $T = 25\text{ }^{\circ}\text{C}$ for silica particles in $[\text{C}_4\text{mim}][\text{BF}_4]$ (A) and in 0.1 mM ($\text{pH} = 9.1 \pm 0.1$) NaCl aqueous solution (mother liquid) (B).

5.3.3 Concentrated Particle Dispersions – Dispersion Microstructure

SANS measurements of dilute nanoparticle suspensions discussed in Chapter 4 Section 4.3.2.3 further quantify the particle size, polydispersity, and coating layer structure and are listed in Table 5.2. As the density of ionic liquid solvation layers is close to the bulk ionic liquid, there is no significant scattering length density difference between solvation layers and the ionic liquid. Therefore, the solvation layers are not detected directly by neutron scattering. However, SANS measurements of a concentration series enable detecting the particle stabilization mechanism through direct measurement of the structure factor.

SANS measurements on more concentrated dispersions of the coated particles in $[\text{C}_4\text{mim}][\text{BF}_4]$ are reported in Figure 5.5, with scattering intensity $I(q)$ versus scattering wave vector q systematically shifted vertically for clarity. With increasing particle concentration, a structure peak becomes evident for $q < 0.01\text{ \AA}^{-1}$. The scattering intensities are analyzed by fitting to Equation 5-7 (defined in materials and

methods section, Section 5.2.3) with an effective structure factor. From these fits, I determine the potential parameters that include an effective particle size and strength of attraction. In the analysis, the particle form factor is accurately represented by a polydisperse core-shell form factor model⁴² with all of the associated parameters measured from the dilute sample for single particle size discussed in Chapter 4.

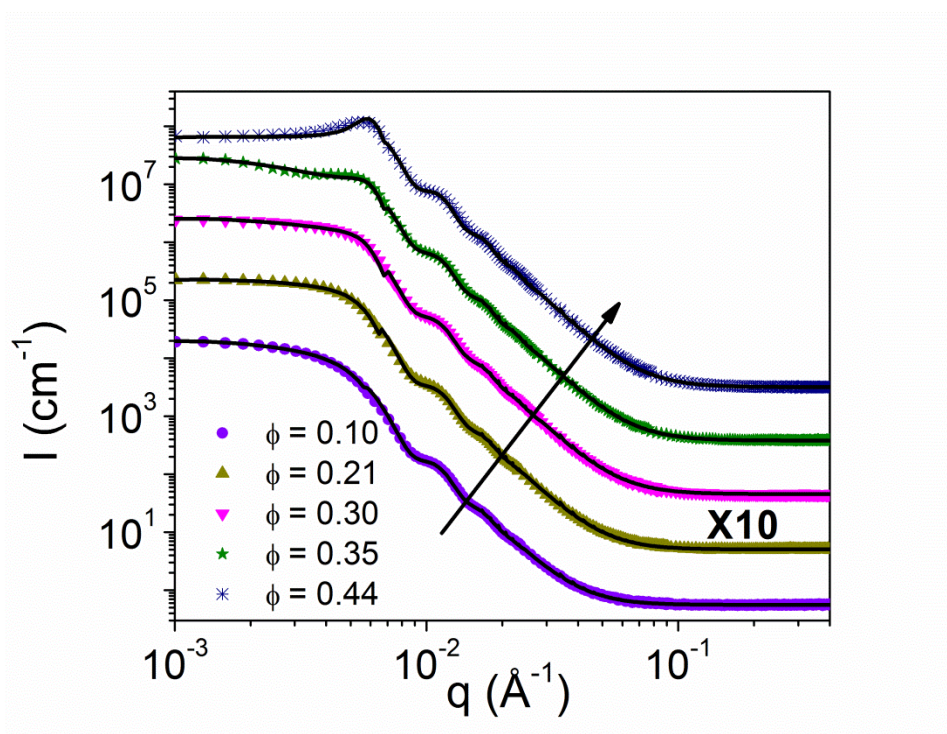


Figure 5.5: SANS intensity I versus scattering wave vector q as a function of particle concentration for 25 °C and the corresponding sticky-hard sphere model fits. (The scattering intensities are systematically shifted by a factor of 10 for clarity.)

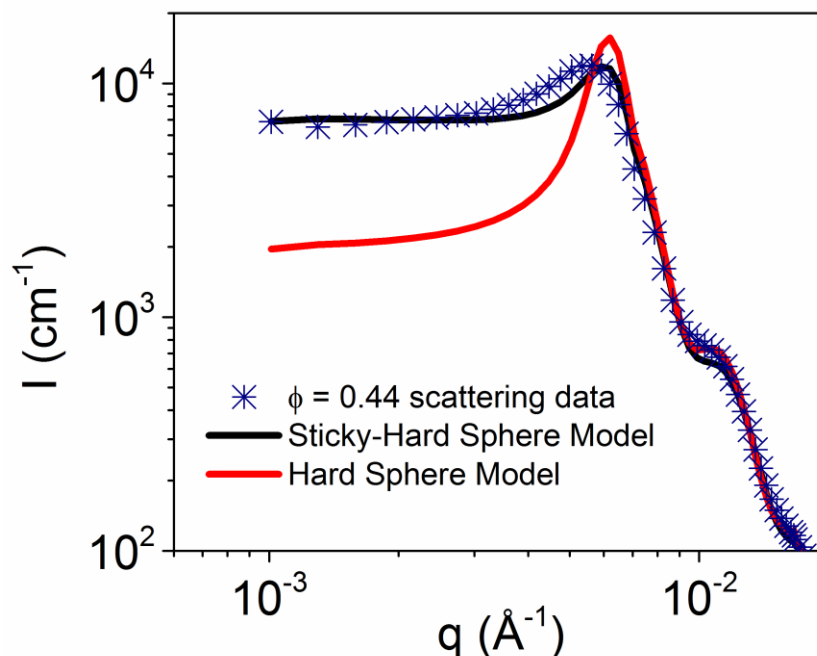


Figure 5.6: The SANS intensity of $\phi = 0.44$ coated particle $[\text{C}_4\text{mim}][\text{BF}_4]$ dispersion with sticky-hard sphere and hard sphere model fits.

The solvation layers detected by DLS should also be evident in the structure factor as they provide steric stability and thus, prevent particles from approaching closely. Consequently, solvation layers will lead to a dispersion structure reflecting this increased, larger particle size. Examination of Figure 5.6 shows that an effective hard sphere potential with an effective radius that includes the solvation layer can capture the location of the intensity peak, but is still not sufficient to describe the suspension microstructure as there are still weak interparticle attractions. To improve the description, I use the simplest model that includes both excluded volume and attractions - the “sticky” effective hard sphere model - and calculate the structure

factor $S(q)$ accordingly.⁴² This structure factor depends on the effective volume fraction (defined in Equation 5-7 in materials and method section, Section 5.2.3) in a self-consistent manner as the number of particles and their effective volume is known in terms of the effective radius. The particles' effective volume fraction can be extracted from the structure factor modeling, keeping the form factor parameters fixed. The sticky hard sphere structure factor fitting parameters and the resultant thicknesses of the solvation layer at each volume fraction are shown in Table 5.4. The solvation layers thickness determined in this manner is slightly less than, but comparable to, the value of 5 nm ascertained from the DLS measurements. Note that the accuracy of the analysis improves with increasing particle concentration as the structure becomes more prominent. Attempts to fit the data with various potential models but without including the solvation shell were unsuccessful to capture the neutron scattering profiles. The increase in effective solvation layer thickness with increasing particle concentration trend is expected in part as close approach of surfaces creates confinement, which can induce more ordering in ionic liquids. It is reported in literature that the solvation layers between confined flat surfaces become more ordered as the surface separation decreases, resulting in a thicker solvation layer.⁴³

Table 5.4: Summary of structure factor fitting parameters for dispersions coated nanoparticles in [C₄mim][BF₄] corresponding to Figure 5.5.

Parameters	$\phi = 0.100$	$\phi = 0.207$	$\phi = 0.295$	$\phi = 0.352$	$\phi = 0.436$
Weight percent	17%	32%	44%	50%	61%
ϕ_{eff}	0.106	0.225	0.340	0.441	0.545
$\bar{r}$ (nm)	54.2	54.2	54.2	54.2	54.2
p	0.105	0.105	0.105	0.105	0.105
δ (shell, nm)	1.2	1.2	1.2	1.2	1.2
$SLD_{core}(A^{-2})$	3.47×10^{-6}	3.47×10^{-6}	3.47×10^{-6}	3.47×10^{-6}	3.47×10^{-6}
$SLD_{shell}(A^{-2})$	3.24×10^{-6}	3.24×10^{-6}	3.24×10^{-6}	3.24×10^{-6}	3.24×10^{-6}
$SLD_{solvent}(A^{-2})$	1.40×10^{-6}	1.40×10^{-6}	1.40×10^{-6}	1.40×10^{-6}	1.40×10^{-6}
Perturbation ε	0.01	0.01	0.01	0.01	0.01
Baxter parameter					
τ	0.70	0.59	0.32	0.16	0.46
Background(cm^{-1})	0.56	0.50	0.45	0.39	0.32
$\bar{r}_{eff}$ (nm)	56.3	56.9	58.1	59.7	59.7
Δr_{solv} (nm)	0.9	1.5	2.7	4.3	4.3

* The effective volume fraction ϕ_{eff} and stickiness parameter τ are set to float during fitting and the other parameters are set to be fixed value. The average effective particle radii $\bar{r}_{eff}$ and solvation layer thickness Δr_{solv} are calculated from effective volume fraction.

The rheological properties of dispersions depend strongly on nanoparticle stability and interparticle interactions, such as solvation layers.¹⁸ Rheological measurements were performed to further explore the effect of the solvation layer formation in the ionic liquid. A suspension of coated nanoparticles dispersed in [C₄mim][BF₄] at moderate concentrations ($\phi = 0.2$) displays near Newtonian behavior, as shown in Figure 5.7. This further confirms their excellent dispersion due to the effect of the coating. The corresponding zero shear and high shear relative viscosity are $\eta_{r,0} = 2.65 \pm 0.05$ and $\eta_{r,\infty} = 2.51 \pm 0.03$, respectively. These viscosities are larger than expected for a hard sphere dispersion based on the silica volume fraction,⁴⁴⁻⁴⁵ as shown in Figure 5-7. Mode coupling theory with $\phi_g = 0.57$ is

employed for hard sphere zero shear relative viscosity,⁴⁵ while the van der Werff correlation with $\phi_m = 0.71$ is used for hard sphere high shear relative viscosity.⁴⁴ The extent of the solvation layer responsible for this increase in viscosity can be deduced from effective particle sizes obtained by fitting the measured zero and high shear viscosities to hard sphere correlations. These values are shown in Table 5.5 and the corresponding solvation layer thicknesses are calculated to be 5.2 ± 0.2 nm and 4.3 ± 0.3 nm, respectively for the dispersion. The results are in good agreement with the previous discussed solvation layer thickness determined by DLS and SANS measurements. Further, the reduction in solvation layer thickness at high shear stress is expected as these layers can be displaced by force; however, the accuracy of this method is not sufficient to draw further conclusions about this reduction.

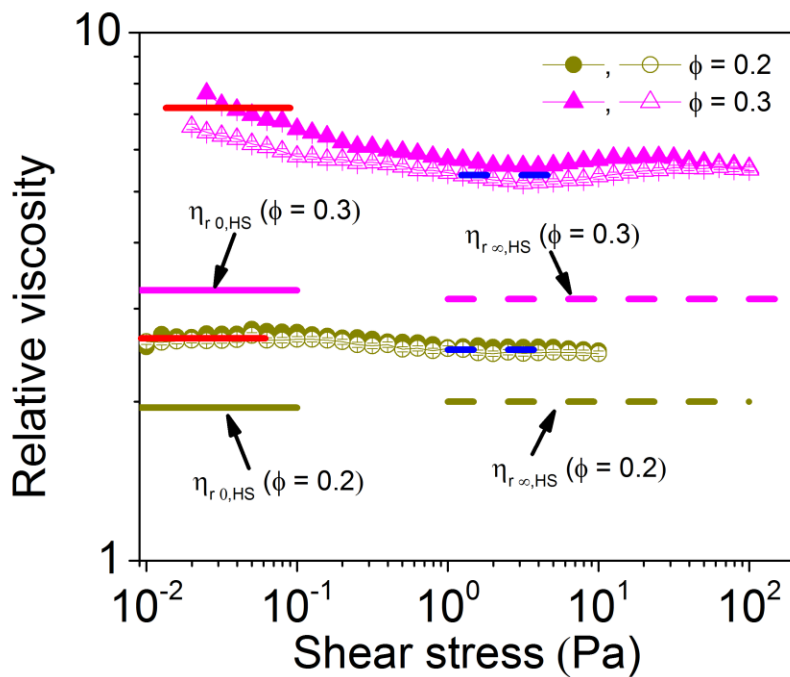


Figure 5.7: Relative viscosity (with error bar) *versus* shear stress for $\phi = 0.2$ and 0.3 stable suspension of fluorocarbon-coated silica nanoparticles in $[\text{C}_4\text{mim}][\text{BF}_4]$. Closed symbols are ascending stress curves and the open symbols are descending stress curves. The solid lines are the corresponding relative zero shear viscosity; the dashed lines are the corresponding relative high shear viscosity.

Interestingly, at higher concentration ($\phi = 0.3$), the suspension shows slightly shear thickening for shear stresses exceeding 4 Pa. This is to be expected for such dispersions with stabilizing layers that are only slightly permeable to the suspending medium, such as solvation layers.⁴⁶⁻⁴⁷ Further, the zero shear viscosity is not well defined and there is some hysteresis in the experiments, both of which are evidence for weak attractive interactions. The same analysis is applied only for the high shear relative viscosity, which is taken as the minimum of the viscosity curve. The

thickness of the solvation layer is estimated to be 5.3 ± 0.2 nm. The corresponding zero shear viscosity is predicted using the effective volume fraction obtained from fitting the high shear viscosity as shown in Figure 5.7, and this value agrees with measured values to within the variation in the data.

These solvation layer thicknesses calculated from rheological measurements are in good agreement with the hydrodynamic radius from DLS and those obtained from SANS structure factor measurements. Interestingly, both the SANS and the rheological measurements suggest the presence of weak attractive interactions that are not expected based on the simple DLVO interaction, suggesting that the van der Waals forces are underestimated for this system.

Table 5.5: Summary of relative viscosity, effective volume fraction and solvation layer thickness calculated from shear flow curves of $\phi = 0.2$ and 0.3 suspensions.

Parameters	$\phi = 0.209$		$\phi = 0.309$	
	Zero Shear	High Shear	Zero Shear	High Shear
$\eta_r (HS)$	1.95	2.00	3.25	3.13
$\eta_r (Measured)$	2.65 ± 0.05	2.51 ± 0.03	$7.34 \pm 0.49^*$	5.46 ± 0.20
ϕ_{eff}	0.274 ± 0.003	0.262 ± 0.002	$0.406 \pm 0.006^*$	0.406 ± 0.006
$\bar{r}_{eff} (nm)$	60.6 ± 0.1	59.7 ± 0.2	$60.7 \pm 0.1^*$	60.7 ± 0.1
$\Delta r_{solv} (nm)$	5.2 ± 0.2	4.3 ± 0.3	$5.3 \pm 0.2^*$	5.3 ± 0.2

* ϕ_{eff} is calculated from high shear relative viscosity of $\phi = 0.309$ dispersion and is used to predict the corresponding zero shear relative viscosity $\eta_r (Measured)$.

5.4 Conclusions

I have demonstrated a method to spontaneously disperse silica particles in ionic liquid $[C_4mim][BF_4]$ by inducing solvent structuring around the surface of the

particle. Extensive characterizations of fluorocarbon (1H,1H,9H hexadecafluoro-1-nonanol) coated silica nanoparticles suspended in ionic liquid [C₄mim][BF₄] using DLS, SANS, TEM, and rheology all confirm the presence of solvation layers of approximately 5 nm. This layer is sufficient to provide steric stabilization against the dispersion attractions. The thickness of this layer is quantitatively similar to that measured for this ionic liquid structuring near flat mica surfaces using surface forces apparatus.^{13, 29} The 5 nm, layer thickness corresponds to seven ion-pair layers, each with 0.7 to 0.8 nm thickness as measured using surface forces.²⁷ The number of layers is also consistent with the measurements of Perkin et al.^{29, 48} on the structuring of [C₄mim][NTf₂] confined between mica.

In much of the analyses presented here it is assumed for simplicity that the solvation layers form a well-defined, uniform shell surrounding the nanoparticles. However, the solvation layers near flat substrates are expected to become less organized and smoothly transition to the bulk liquid, as shown by surface force apparatus (SFA),²⁹⁻³⁰ atomic force microscope (AFM) measurements,^{13, 25, 43} and simulations⁴⁹. Closer examination of the variations in shell thickness determined at varying particle concentrations and shear rates, and comparison of dynamic and static measurements, suggests that a more detailed analysis can provide further information about the nanostructure of this solvation layer. The molecular structure for confined layers of related ionic liquids have been proposed based on surface forces measurements and molecular packing parameters.³⁰ Such an analysis will require a full theory for the dispersion forces and electrostatic forces acting between highly curved surfaces, such as those of the nanoparticles, with such nanostructured solvation layers, which goes well beyond the scope of this work. The comprehensive data

presented here, collected using a variety of measurement techniques, not only provides a database with which such theories can be rigorously tested, but also acts as guidance for the development of future theories.

Molecular design of a surface coating to induce specific molecular interactions between the particle surface and the ionic liquid with the intent to create solvent structuring is demonstrated as a method to create spontaneous dispersion and stabilization of nanoparticles that are otherwise not dispersible in ionic liquids. The resultant solvation layers impart colloidal stability, but also lead to larger effective volume fractions in solution. The presence of ubiquitous dispersion forces and the solvation layer will ultimately limit the total concentration of particles dispersible in the ionic liquids; however, I have successfully dispersed these particles up to 61 wt% (corresponding to 45 vol%), which is a significant improvement on the current published maximum of 20 wt% silica particle content.

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Chapter 6

ALCOHOL COATED PARTICLE SYSTEM – SHEAR THICKENING, AND THERMAL RESPONSE

In this chapter, I describe a successful attempt to formulate stable nanoparticle dispersions in ionic liquids that exhibit significant shear thickening through designing the surface coating of particles (alcohol coating). A stable dispersion of silica nanoparticles in ionic liquid $[C_4mim][BF_4]$ that exhibits significant shear thickening is formulated by controlling the strength of hydrogen bonding between the nanoparticle surface and the anion of $[C_4mim][BF_4]$. Colloidal stability is demonstrated to be caused by the formation of solvation layers, the properties of which are determined from scattering measurements. Time-temperature superposition measurements and the onset of yielding behavior in steady shear indicate the increase of particle-particle attraction and loss of stability of colloidal dispersions above 30 °C. Small angle neutron scattering (SANS) and dynamic light scattering (DLS) measurements confirm the reduction in solvation layering at elevated temperatures, leading to a transition from stable dispersion to unstable, attractive gel at increased temperature (*i.e.*, an inverse melting transition). Thus, controlling specific surface-anion interactions through chemical functionality can be used to formulate nanoparticle dispersions in ionic liquids with specific rheological properties. Text and figures are reproduced and adapted with permission from Gao J., et al. *Journal of Rheology* 2016 (submitted).

6.1 Introduction

Stable, concentrated colloidal suspensions that exhibit a reversible increase in viscosity when subjected to increasing shear rate are known as shear thickening fluids (STFs).¹⁻² This shear thickening transition is the result of a competition between hydrodynamic and stabilizing forces, such that a rearrangement of the microstructure occurs during strong shear flow. At high shear rate/stress, colloidal suspensions are dominated by short-range lubrication interactions that lead to density fluctuations of particle during shear and ultimately, stress-bearing clusters named as “hydroclusters”.³ Control of shear thickening in colloidal dispersions is relevant to numerous industrial products and processes, such as paints, lubricants, pharmaceutical, as well as protective materials such as “soft” body armor.⁴ Typical shear thickening fluids are formulated in molecular solvents, such as polyethylene glycol (PEG) or ethylene glycol (EG) as carrier medium. Recently, it was reported that stable concentrated silica particles in room temperature ionic liquids (ILs) dispersions display reversible shear thickening under high shear rate/stress.⁵⁻⁶ Room temperature ILs are organic salts in the liquid state at room temperature, which are comprised entirely of ions.⁷⁻⁸ Due to the unique physicochemical properties of room temperature ILs, such as low melting temperature and negligible vapor pressure, IL dispersed shear thickening fluids can be used in extreme environments compared to PEG/EG based STFs, such as applications as field-responsive nanocomposites for protecting astronauts against hazards from micrometeorite and orbital debris (MMOD).⁹⁻¹⁰

The rheological response of colloidal dispersions strongly depends on particle stability and microstructure. Particle stabilization in ILs is challenging because their ionic nature screens electrostatic repulsive forces. Thus, not surprisingly, it has been reported that particle dispersion and stability in ILs depends on the specific chemical

composition of the ILs as well as the surface chemistry of the particles.^{5-6, 11-13} The first report of suspension rheology in ILs was for Hematite colloids in ethyl-methylimidazolium ethylsulfate, where a stable, Newtonian dispersion was observed for lower particle loadings, but a yielding dispersion was observed at higher loadings, without shear thickening.¹¹ Hydrophilic fumed silica particles were investigated to be well dispersed in [C₄mim][BF₄] displaying shear thickening.⁵ However, such dispersions were unstable in 1-ethyl-3-methylimidazolium bis(trifluoromethane sulfonyl)-amide ([C₂mim][NTf₂]) and the dispersions exhibited a yielding behavior and strong shear thinning.⁵ In addition, aggregation and gelation were reported for hydrophobic fumed silica particles in [C₄mim][BF₄],⁵ demonstrating that it is not trivial to disperse particles into ILs.

In the original work by Altin *et al.*, the authors point to the unique properties of ILs with respect to their nanoscale structure, such that particles, *i.e.* the hematite, can be stabilized in solution by structured solvent surrounding the particles.¹¹ This picture was formalized by Ueno *et al.*⁵ and proven experimentally by Gao *et al.*⁶ The stability of fumed hydrophilic silica particles in [C₄mim][BF₄] in the absence of any stabilizer^{5, 14-15} is due to the presence of solvation forces arising from solvent structuring near the particle surfaces.^{6, 14-16} Derjaguin-Landau-Verwey-Overbeek (DLVO) theory, which accounts for van der Waals attraction and electrostatic repulsion between particles in solution,¹⁷ was used to evaluate the interaction between particles in dispersions. The high ionic strength in ILs effectively screens the electrostatic repulsion between silica particles,¹⁸⁻²⁰ resulting in loss of stability of the particles in ILs by the van der Waals attraction between particles.^{6, 21} However, stability can be imparted by inducing solvation layers to form around particles through suitably functionalizing the surface

to generate hydrogen bonds with the anion of the IL. This couples to the nanostructure in the IL to create alternating layers of anions and cations that are known as solvation layers. Such ionic ordering of the solvent propagates some distance into the IL and provides a repulsive force acting between two particle surfaces dispersed in the IL. This was hypothesized as the mechanism for stabilizing fumed silica dispersed in [C₄mim][BF₄], where surface silanol groups hydrogen bond with the anion and create solvation layers provide sufficient repulsion against the weak van der Waals attractions of porous aggregated fumed silica particles.⁵⁻⁶ Indeed, solvation forces have been confirmed and measured both between macroscopic surfaces and colloidal particles in ILs. Distant-dependent solvation forces have been observed between macroscopic mica or silica surfaces in both protic and aprotic ILs by surface force measurements.²²⁻²⁷ These reports are also consistent with molecular dynamics simulation results of solvation layers formation driven by specific ion-surface interactions.²⁸ Both measurements and simulations indicate that the ion pairs are arranged in a layered structure near the solid surfaces.^{6, 26} Solvation structuring in ILs around nanoparticle surfaces was also measured directly on spherical silica particles purposefully surface functionalized with fluorinated hydrocarbons to disperse in an aprotic IL.⁶ The hydrogen bonding between the fluorinated anion of the IL [C₄mim][BF₄] and the terminal hydrogen atom on the surface coating drives the formation of solvation layers that impart colloidal stability by steric repulsion. The thickness of solvation layers was determined to be approximately 5 nm at room temperature by transmission electron microscopy (TEM), rheology, DLS, and SANS.⁶ Importantly, such surface solvation layers, being just surface-organized structures comparable to the sponge-like structure in the IL itself, are thought to be fluid-like in

the direction parallel to the solid surface.²⁹ Consequently, they act to stabilize the dispersion but mitigate the shear thickening response.

Grafting polymer to the particle surface can also improve suspension stability in ILs^{16, 21} if the IL is a good solvent for the polymer. It was reported that poly(methyl methacrylate) (PMMA)-grafted silica nanoparticles show good dispersion in 1-butyl-3-methylimidazolium hexafluorophosphate ([C₄mim][PF₆]) and 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C_nmim][NTf₂]), presumably because PMMA is itself soluble in this IL; however, such coated particles show poor dispersion if PMMA is insoluble in the IL (*e.g.*, [C₄mim][BF₄]).²¹ Similar phenomenon can be found for grafting polyelectrolytes, such as poly(acrylic acid) (PAA) coated maghemite nanoparticles in a protic IL ethylammonium nitrate (EAN).³⁰ The stability of the nanoparticles was controlled by tuning the pH through changing the solvation quality of EAN for the polymer chains comprising the coating on the particles.³⁰ PAA-coated particles are stable at acidic pH, when coated polymer chains are fully protonated and can provide steric repulsive interactions. At basic pH, polymer chains are deprotonated due to the poor solvation quality of EAN, resulting in the aggregation of coated particles. For both of the cases, the mechanism of stability is afforded by the steric repulsion between the grafted layers of significant extent and as is typical with such systems, the system will become unstable when the brush is immersed into a poor solvent and collapses.² The stability provided by surface grafted polymers through steric repulsion is reported to be thermal-sensitive. Poly(benzyl methacrylate) (PBnMA)-grafted silica nanoparticles^{16, 31} were stabilized in [C₂mim][NTf₂] through steric forces. Highly concentrated suspensions formed stable soft glassy colloidal dispersion at low temperature; however, a temperature-induced

colloidal glass-to-gel transition was observed with a discrete change in the color of dispersion with increasing temperature. The particle interaction changed from repulsive to attractive with increasing temperature, as deduced from the non-monotonic behavior of the viscosity.^{16, 31} However, such polymer-stabilized dispersions do not exhibit shear thickening rheology in the regimes studied presumably due to the strong nanoscale repulsive forces afforded by the well-solvated polymer brush.³²⁻³³

This concise literature summary of particle dispersions in ILs suggests a hypothesis that by controlling the strength of anion-colloid interactions, I can induce solvation layering sufficient to provide steric stability but not to an extent that suppresses shear thickening at reasonable shear rates. In this study, I test this hypothesis by studying the temperature dependence of solvation layering and the rheology of a model dispersion of coated silica particles in a typical, aprotic IL [C₄mim][BF₄]. The effect of solvation layers thickness on shear rheology is investigated by comparing silica particles with varying surface functionality designed to vary the strength of hydrogen bonding with the IL anion.⁶ Furthermore, high temperature is used to weaken this hydrogen bonding and hence, reduce the solvation stabilization, leading to a loss of shear thickening and eventually, gelation and an inverse melting transition. Particle aggregation due to the loss of stability at high temperatures is confirmed directly by DLS measurements. SANS measurements are used to investigate the corresponding solvation layers and particle interaction change with temperature. As will be shown, this dramatic transition in rheological behavior is explained by the strength of attraction between the particles as controlled by the extent

of solvation layering induced by temperature sensitive hydrogen bonds between surface coating and anion group $[\text{BF}_4]^-$ of $[\text{C}_4\text{mim}][\text{BF}_4]$.

6.2 Materials and Methods

6.2.1 Materials

The IL $[\text{C}_4\text{mim}][\text{BF}_4]$ (99% pure, Iolitec, $\rho_m = 1.201 \text{ g/cm}^3$, $\eta_m = 101.4 \text{ mPa} \cdot \text{s}$), was dehydrated in vacuum oven at 70°C for 24 h prior to use. The final water content was 373 ppm as determined by the Karl Fischer titration. The rheological properties of this IL and its sensitivity to water have been reported elsewhere.³⁴ Silica nanoparticles (Seahostar KE-P10, Nippon Shokubai Co., Tokyo, Japan) of radius $a = 60 \text{ nm}$ and particle density $\rho_p = 1.89 \pm 0.02 \text{ g/cm}^3$ ³⁵ were used to prepare colloidal dispersions. The volume fraction is calculated using these densities. KE-P10 silica particles contain $\sim 10\%$ organic alcohol as surface functionalization according to the manufacture.³⁶ The nanoparticles were dispersed in the dehydrated IL at varying concentrations from dilute through concentrated. The colloidal dispersions were mixed using a roll mixer for one week to insure homogeneity throughout the sample, followed by a 5 min degassing to remove air bubbles in the samples. As the particle stability and structure of solvation layer are sensitive to water,³⁷⁻⁴⁰ silica particles were dried in oven at 80°C for 10 h before dispersing in $[\text{C}_4\text{mim}][\text{BF}_4]$ and the dispersions were dehydrated again in a vacuum oven at 50°C for 24 h prior to each measurement. The water contents of dispersions were about 1000 ppm as measured by Karl Fischer titration.

6.2.2 Rheology

Rheological measurements were performed on a stress controlled Discovery Hybrid Rheometer (DHR) (TA Instruments, New castle, DE) with Peltier plate temperature control, and a 40 mm stainless steel cone with 2° cone angle with solvent trap. To erase any previous shear histories and maintain a consistency between measurements, a steady pre-shear was applied at a shear stress of 10 Pa for 2 min before each dynamic rheological measurement. Samples were stable and reproducible during the measurements as determined by comparing the properties during this pre-shear step. Prolonged exposure to the atmosphere (~days) will induce significant rheological changes primarily due to the strong effect of small amounts of water on the rheological properties of the IL.³⁴

6.2.3 Dynamic Light Scattering (DLS)

The hydrodynamic radius R_H of the particles are determined from the intensity autocorrelation function (IACF) of dilute dispersions measured using a Brookhaven Instruments ZetaPals DLS instrument at 10 °C to 60 °C. The IACF is modeled using the Stokes-Einstein-Sutherland equation and assuming diffusive behavior. Measurements are performed after 10 min temperature equilibrium at each temperature. The incident photon laser wavelength is $\lambda = 658$ nm and the scattered light intensity was detected at a scattering angle $\theta = 90^\circ$. The DLS instrument setup, measurement protocol and analysis method follow prior protocols.⁶

6.2.4 Small-Angle Neutron Scattering (SANS)

SANS measurements were performed at the National Institute of Standards and Technology (NIST) Center for Neutron Research (NCNR) in Gaithersburg, MD on NGB30 beamline. Samples were loaded into demountable titanium cells with a 1 mm

path length. The cell temperatures were maintained to ± 0.1 °C using the 10 position sample cell holder with fluid bath. A wide range in scattering wavevector q was obtained by combining scattering intensity from four different instrument configurations at detector distances of 1, 4, 13, and 15.3 m with lens. The wavelength for 1, 4, and 13 m configurations is 6.0 Å and 8.0 Å for 15.3 m with lens. The SANS scattering intensity profiles were reduced to absolute scale and analyzed with the NIST data reduction and analysis macros in IGOR Pro available from NIST.⁴¹ The total background was calculated from the slope of the Porod plot (Iq^4 versus q^4), and subtracted from all SANS spectra.

The SANS profiles are analyzed by IGOR software.⁴¹ Properties of the dispersions were determined by fitting the measured SANS intensity using a form factor model for Schultz distributed sphere particles and a monodisperse structure factor model that includes hard core repulsion with contact attraction (sticky-hard sphere model). More details about the models employed are provided in Chapter 5.⁶

6.3 Results and Discussion

6.3.1 Steady Shear and Shear Thickening

The ascending steady state viscosity curves of the $\phi = 0.4$ dispersion in [C₄mim][BF₄] over a broad range of temperatures are compared in Figure 6.1. I observed that the ascending and descending flow curves overlap without hysteresis at low temperatures (10 °C to 30 °C). However, at high temperatures above 40 °C, the flow curves no longer overlap and exhibit hysteresis. Nonetheless, the flow properties are thermal-reversible and no permanent particle aggregation is observed during thermal cycling.

At lower temperatures, from 10 °C to 30 °C, the colloidal dispersion displays a shear rheology characteristic of a stable dispersion of near-hard sphere particles, as reported previously for dispersions of these particles in various molecular solvents.³⁵ A marked shear thickening behavior is observed, which is more pronounced than for related particles with different surface functionality dispersed in the same IL medium.⁶ With increasing temperature, the dispersion viscosity decreases systematically due to the decrease of IL viscosity, but the shear thickening property is still evident. However, at 40 °C, this shear thickening behavior becomes less evident as there is a substantial increase in viscosity at low shear rates. Above 40 °C, shear thickening is not observed for this colloidal dispersion and the low shear viscosity grows dramatically, signaling the onset of a weak yield stress. The presence of shear thinning and yielding at these higher temperatures is characteristic of gelation or inverse melting,⁴² which suggests stronger attractions between particles leading to particle aggregation at these higher temperatures.

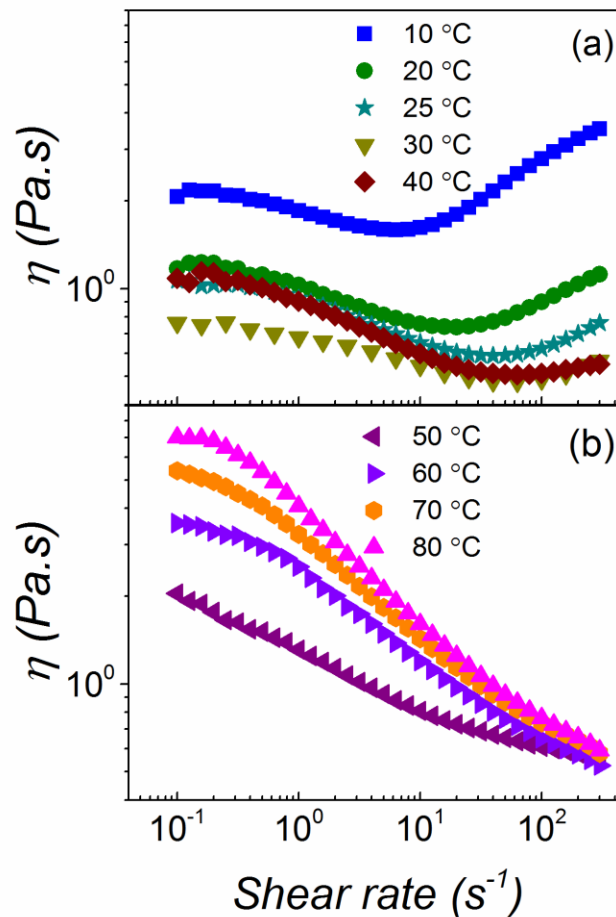


Figure 6.1: Steady shear viscosity as a function of shear rate for colloidal dispersion = 0.4 silica particle – [C₄mim][BF₄] at (a) low temperatures and (b) high temperatures. Viscosity data are acquired with ascending shear rate.

The variation in the thermal-rheological response is more evident by plotting the relative viscosity as a function of Péclet number (Pe) and shear stress, as shown in Figure 6.2. At low temperatures, the flow curves (10 °C to 30 °C) overlap with each other, as expected for Brownian suspensions governed largely by hydrodynamic

interactions.⁴³ It is evident that the onset of shear thickening occurs at a nearly constant value of shear stress independent of temperature over this range. The onset of shear thickening in colloidal dispersions has been well studied and is shown to be stress-controlled.^{3, 44} Furthermore, the stress at the onset of shear thickening is a strong function of the particle size, such that the steady shear rheological data suggest the same particle size at these low temperatures. Remarkably, these overlapping curves also are in quantitatively consistent with the flow curve of the $\phi = 0.4$ dispersion of KE-P10 silica particle in PEG-200,³⁵ which is shown in Figure 6.2. That the flow curves are nearly identical for the silica particles dispersed in both PEG-200 and [C₄mim][BF₄] is an evidence of a stable silica nanoparticle dispersion in this IL over this temperature range.

When shown in a dimensionless plot such as Figure 6.2, the viscosity behavior of the dispersion above 30 °C is observed to increase dramatically relative to that expected for dispersions of near hard-spheres. Strong shear thinning behavior is evident at these higher temperatures. This is typical of weak gelation,² and is characteristic of strong inter-particle attractions at higher temperatures.⁴⁵ The onset of gelation and the loss of shear thickening in the regime of flow explored is consistent with a loss of stability of the silica particles in [C₄mim][BF₄] at these elevated temperatures. This is postulated to be induced by a loss of the solvation layer structure, which will be discussed in Section 6.3.3. Note, however, that decreasing the temperature restores the dispersion to its flowable, shear thickened state such that the gelation is thermo-reversible, but with an inverse temperature behavior of ‘normal’ gelation.

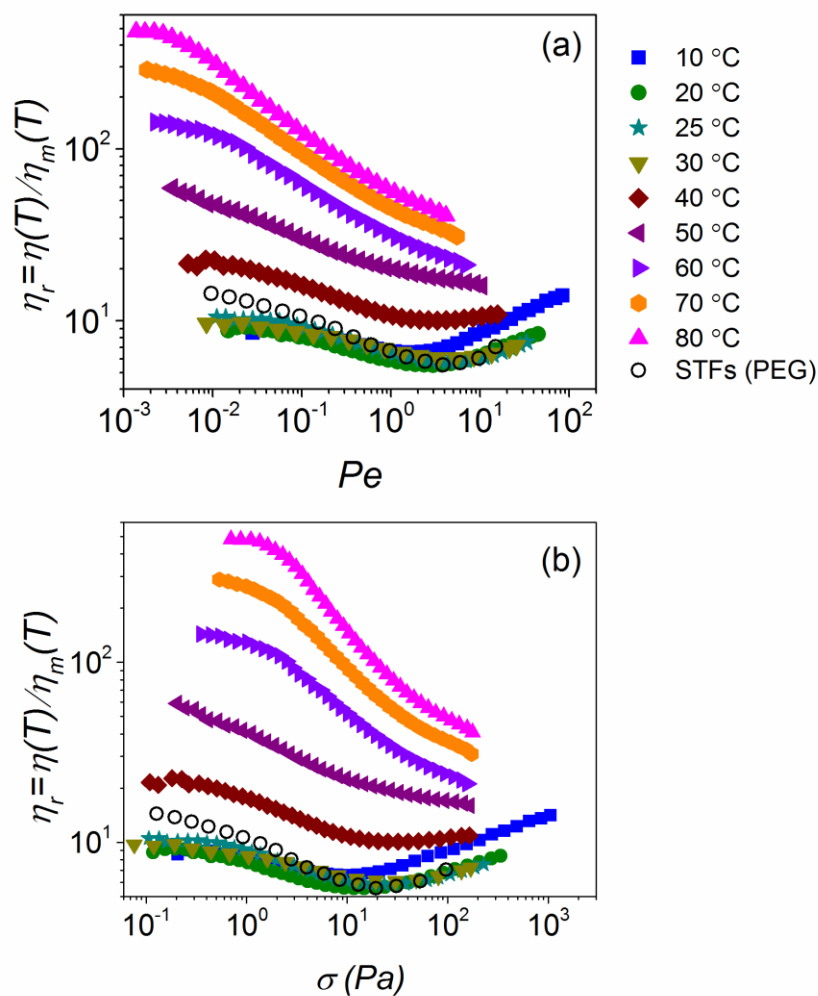


Figure 6.2: Steady shear relative viscosity as a function of Pe and shear stress of $\phi = 0.4$ silica particle – $[C_4mim][BF_4]$ dispersion at different experimental temperatures. The relative viscosity curves are compared with the flow curve of $\phi = 0.4$ dispersion of same silica particles in polyethylene glycol (PEG-200) at 25 °C.³⁵

Importantly, these dispersions exhibit a stronger shear thickening than previously reported for fluorocarbon coated silica nanoparticles⁶ dispersed in the same IL at the same volume fraction $\phi = 0.4$ at 25 °C, as shown in the comparison plotted

in Figure 6.3. The critical shear stress for shear thickening of the dispersions of fluorocarbon coated silica particles in [C₄mim][BF₄] is consistent with the KE-P10 silica particle dispersions in [C₄mim][BF₄] as well as for dispersions in PEG-200, which is expected due to the similar particle sizes (~100 nm in diameter).³ However, it is evident that the shear thickening strength of fluorocarbon coated silica particle dispersion is weaker than the KE-P10 silica particles in [C₄mim][BF₄] and PEG-200 of volume fraction $\phi = 0.4$. The separation between hydroclustered particles in the shear thickened state is on the order of a nanometer for these colloidal dispersions, such that shear-thickening directly probes the nanoscale forces acting between particle surfaces.⁴⁶ For example, it has been reported that polymer grafted or adsorbed onto the particle surface can delay or even suppress shear thickening.^{1, 32-33, 37} In our systems, solvation layers of highly organized ionic liquid forming on the particle surface provide steric repulsion and particle stability in a manner similar to the steric repulsion arising from a grafted/adsorbed polymer brush. Consequently, it can be postulated that difference in shear thickening strength, compared to the fluorocarbon coated silica particle system, is a consequence of differences in the range and strength of the repulsive forces created by the solvation layers on the nanoscale. To further explore this hypothesis, some further insights about the thermal properties of the solvation layers can be obtained from linear viscoelastic measurements, as described next.

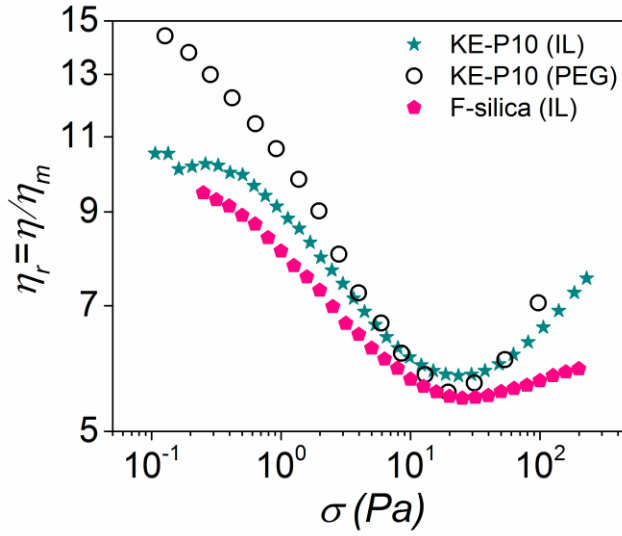


Figure 6.3: Comparison of steady shear relative viscosity of KE-P10 – [C₄mim][BF₄] dispersion, KE-P10 – polyethylene glycol (PEG-200) dispersion,³⁵ and fluorinated silica particle – [C₄mim][BF₄] dispersion⁶ of same volume fraction $\phi = 0.4$ at 25 °C.

6.3.2 Linear Viscoelasticity

The dynamic linear viscoelastic moduli of the $\phi = 0.4$ silica particle – [C₄mim][BF₄] dispersion are shown in Figure 6.4a for the temperatures corresponding to Figure 6.2. The loss modulus G'' is always larger than the storage modulus G' , indicating the dispersion is governed by the hydrodynamic forces for all frequencies studied in this paper.⁴⁷ Using time-temperature superposition method for colloids as described by Shikata and Pearson,⁴⁷ after subtracting off the high frequency limiting viscosity η'_∞ , the moduli are shifted by a horizontal shift factor a_T onto a master curve with the reference temperature ($T_{ref} = 25$ °C), as shown in Figure 6.4b. The horizontal shift factors a_T for each temperature are defined in Figure 6.5 and compared with the ratio of the viscosity of dispersion medium [C₄mim][BF₄] at the experimental temperature to the viscosity of [C₄mim][BF₄] at the reference temperature $T_{ref} = 25$ °C.

It has been demonstrated that hard-sphere colloidal suspensions governed by thermodynamic and hydrodynamic forces can be scaled by the viscosity of the suspending medium.⁴⁷ As shown in Figure 6.5, the shift factor a_T scales with the viscosity of the medium [C₄mim][BF₄] over the temperature range from 10 °C to 30 °C. This confirms that the linear response of the dispersion scales with the viscosity of the dispersion medium, and that the inter-particle interactions are not affected by changing temperature from 10 °C to 30 °C. However, for 40 °C and above, the shift factors are nearly constant with temperature, and importantly, significantly larger than would be expected from the thermal dependence of the medium viscosity. These deviations indicate a fundamental change in the particle-particle interaction with increasing temperature above 30 °C, which is consistent with the steady shear results. Importantly, the relative high frequency viscosity $\eta'_{r,\infty}$ exhibits the same qualitative trends, as evident in Figure 6.5. From 10 °C to 30 °C, the relative high frequency viscosities are nearly constant due to the liquid state of dispersion at these temperatures, while the relative high frequency viscosity $\eta'_{r,\infty}$ increases with increasing temperature above 40 °C. This is attributable to the presence of aggregation and gelation of the dispersion at high temperatures.

Both the steady shear and small amplitude oscillation shear rheology results indicate a stable and near-hard sphere silica colloidal dispersion in [C₄mim][BF₄] at temperatures between 10 °C to 30 °C, and loss of stability above 30 °C. At lower temperatures, this IL based dispersion displays strong shear thickening, which is comparable to that for a similar dispersion in PEG-200 at the same solid volume fraction. In the following, the dispersion microstructure and inter-particle interactions will be explored by SANS measurement to understand the mechanism behind the

strong shear thickening properties at room temperature and the cause of the loss of stability of silica colloids at higher temperatures.

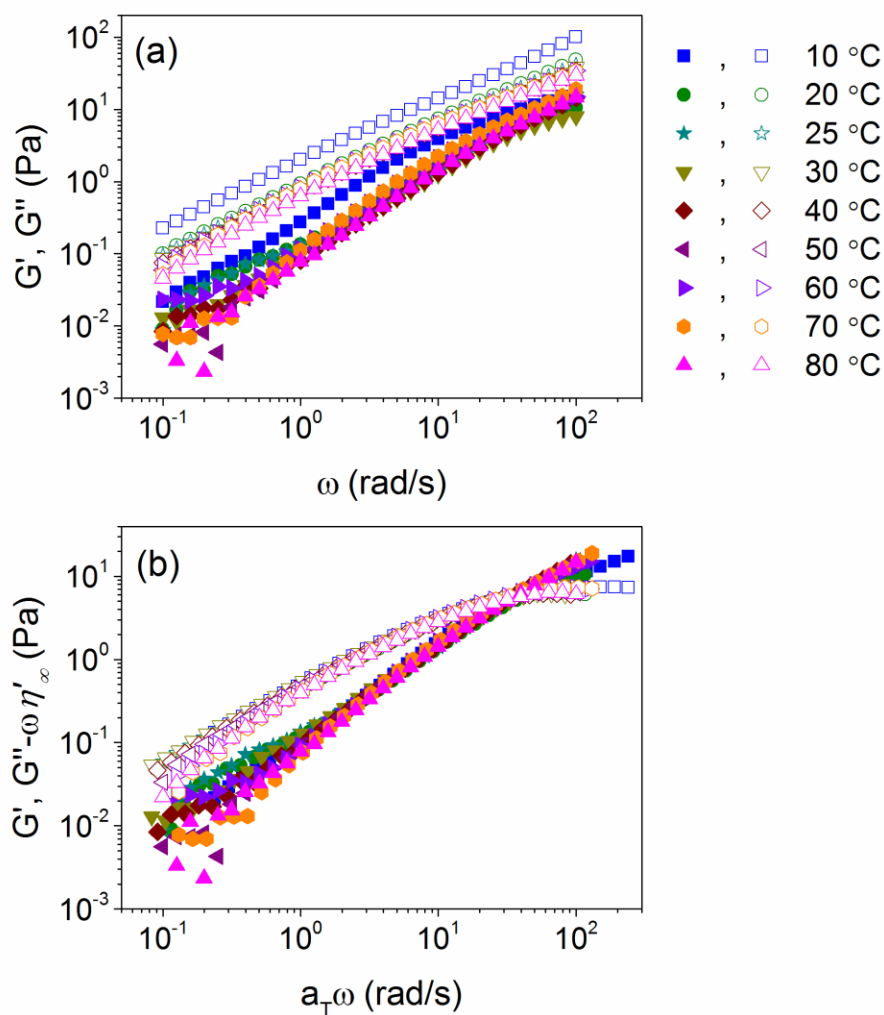


Figure 6.4: (a) Dynamic moduli of $\phi = 0.4$ silica particle – $[C_4mim][BF_4]$ dispersion at different temperatures; and (b) shifted dynamic moduli curves according to time-temperature superposition (TTS) described by Shikata and Pearson.⁴⁷ The closed symbols represent storage modulus G' and open symbols represent loss modulus G'' (a) or subtracted $G'' - \omega\eta'_\infty$ (b).

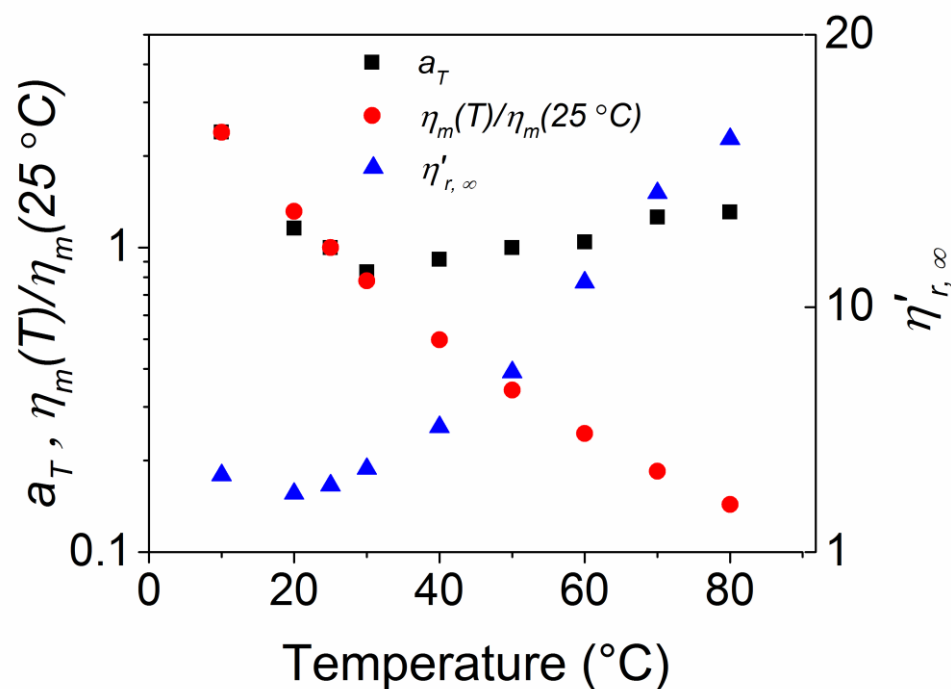


Figure 6.5: Shift factors a_T and viscosity change of $[\text{C}_4\text{mim}][\text{BF}_4]$ referenced to 25 °C (left y axis) and relative high frequency limiting viscosity $\eta'_{r,\infty}$ (right y axis) of $\phi = 0.4$ silica particle – $[\text{C}_4\text{mim}][\text{BF}_4]$ dispersion at various temperatures.

6.3.3 Inter-Particle Interaction and Dispersion Structure

The form factor of the KE-P10 silica particle is measured by small angle neutron scattering (SANS) using dilute dispersions in deuterated water D_2O and $[\text{C}_4\text{mim}][\text{BF}_4]$ at 25 °C and plotted in Figure 6.6a. As expected, the general shapes of the scattering profiles are similar due to the same dispersed silica particle core. Both scattering intensity profiles are fit well by a Schulz - distributed polydisperse sphere model using the same protocol to fit the particle size, polydispersity, and volume fraction as used previously for the fluorocarbon coated silica particle system.⁶ These fits yield a particle radius of 62 nm and polydispersity of 10%. As stated in our

previous study for the fluorocarbon coated silica particle system, the solvation layers around the particle surface are not detectable by neutron scattering due to the similar density of the solvation layers as compared with the bulk IL. However, the presence of solvation layers increases the effective hydrodynamic particle size of the particles, which leads to a slower diffusion rate when dispersed in [C₄mim][BF₄] that can be measured by dynamic light scattering (DLS).⁶ The hydrodynamic radius of silica particles in H₂O and [C₄mim][BF₄] as measured using DLS are listed in Table 6.1. There is an obvious increase in the hydrodynamic radius when the particles are dispersed in [C₄mim][BF₄], as compared with water. The increase of hydrodynamic radius (~3.5 nm) in [C₄mim][BF₄] as compared to water is a consequence of solvation layers forming around silica particle surface.

The solvation layers detected by DLS should also be evident in the structure factor as they provide steric stability and thus, prevent particles from approaching closely. Consequently, solvation layers will lead to a dispersion structure reflecting this larger effective particle size due to the solvation layers. The structure factor of KE-P10 silica particles in [C₄mim][BF₄] is measured using SANS applied to concentrated particle dispersions. The scattering profiles of KE-P10 silica particles in [C₄mim][BF₄] at various concentrations at 25 °C are plotted in Figure 6.6b. A structure peak at $q < 0.01 \text{ \AA}^{-1}$ becomes evident with increasing particle concentration, as expected. The scattering intensities are fitted by a “sticky” effective hard sphere structure factor model and the particle form factor model with parameters determined from the dilute particle solutions, as shown in Figure 6.6a. The effective volume fraction of particles in suspensions can be extracted from the structure factor, and thus, the effective particle size can be determined. The fitting method follows the same

procedure as for fluorocarbon coated silica particle system.⁶ From these measurements, the solvation layer thickness is determined to be 2 – 3 nm, which is slightly smaller but comparable to the layer thickness of 3.5 nm from DLS experiments.

The 3 nm-thick solvation layers on KE-P10 silica particles in [C₄mim][BF₄] are thinner than the solvation layers formed for fluorocarbon coated silica particles in the same IL. This decrease in solvation layer thickness can be attributed to weaker hydrogen bonding between the anion [BF₄]⁻ and the KE-P10 particle surface. KE-P10 silica particles are coated by an alcohol.³⁶ The resultant carbon chain coating is expected to form weak hydrogen bonds with the anion group [BF₄]⁻. For example, the strength of hydrogen bonds between 4-carbon chain alcohol and the ion F⁻ is ~42 kJ/mol, however, the strength increases by 3 times (~127 kJ/mol) for a 2-carbon chain fluorocarbon.⁴⁸ In general, the strength of hydrogen bonds also increases with longer fluorocarbon chain length.⁴⁸ Thus, I can estimate the strength of hydrogen bonds for KE-P10 particles in the IL to be at least 3 times weaker than those of the fluorocarbon coated particles. The weaker hydrogen bonds between alcohol surface coating and [BF₄]⁻ anion group of [C₄mim][BF₄] will result in a thinner solvation layer.

Importantly, the thinner solvation layers (~ 3 nm) are responsible for the stronger shear thickening strength as compared to fluorocarbon coated silica particle dispersions with thicker solvation layers (~ 5 nm). It was found that shear thickening can be suppressed by grafting polymer layer or brush onto the particle surfaces, which imposes a repulsive force that prevents the particles from approaching each other.^{1, 37} This effect increases progressively as the brush thickness on the particle surface increases. When the thickness of brush approaches 10% of the particle radius, the

shear thickening is effectively eliminated. Solvation layers initiated by hydrogen bonds around silica particles play the same role as the polymer brushes providing a repulsive force to prevent the aggregation of silica particles. That is, this thicker solvation layer suppresses the shear thickening by suppressing the formation of “hydroclusters” under high shear. For the fluorinated carbon coated silica particles, the thickness of solvation layers is approximately 5 nm, which reaches 10% of the silica particle radius. Thus, shear thickening of dispersions are strongly suppressed with only slightly viscosity increases at high shear stress. The coated silica particles KE-P10 have solvation layers (~ 3 nm) in the IL that are $\sim 5\%$ of particle radius, and concentrated dispersions show enhanced shear thickening at room temperature.

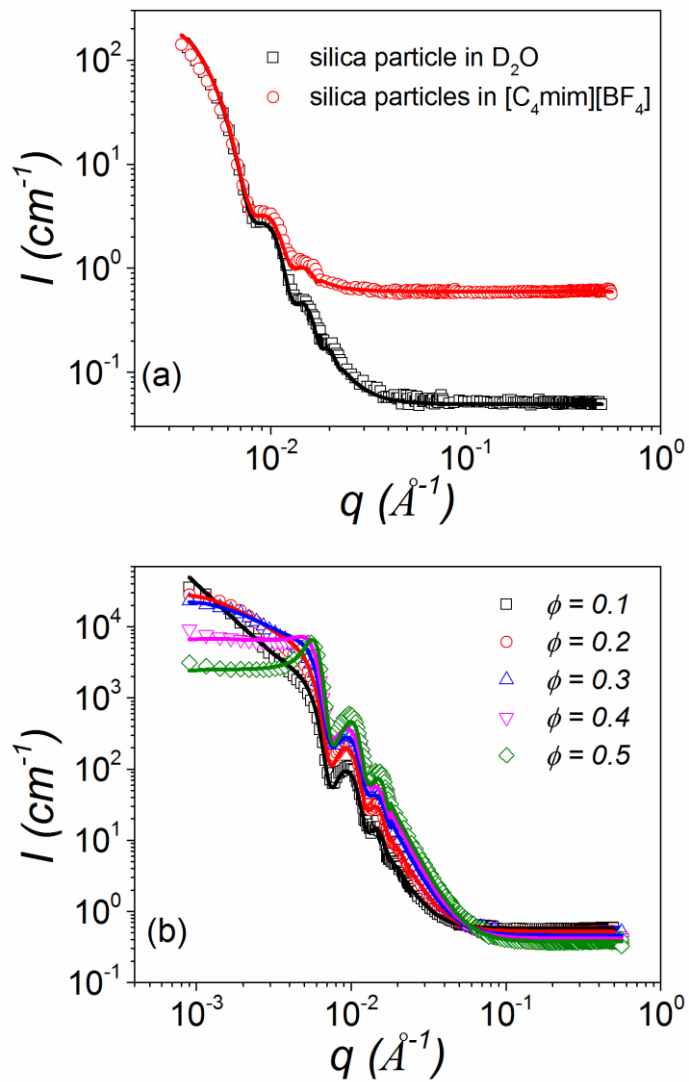


Figure 6.6: SANS profiles of (a) dilute silica particles in D_2O and $[C_4mim][BF_4]$ solvents with Schulz-distributed sphere form factor model fitting; (b) silica particles in $[C_4mim][BF_4]$ of various concentrations with “sticky” hard sphere structure factor model fitting at 25 °C.

Table 6.1: Summary of particle radii of silica particle in different solvents at 25 °C using various methods.

Measurement Techniques	Particle in water	Particle in [C ₄ mim][BF ₄]
DLS	63.4 ± 4.9 nm	66.9 ± 3.7 nm
SANS	62.0 ± 6.2 nm <i>p</i> = 10 %	62.0 ± 6.2 nm <i>p</i> = 10 %

To explore this effect further, DLS measurements were performed for the particles in very dilute solution in the IL (0.1 vol %) over the temperature range of interest. The intensity averaged radii and the associated standard deviations are plotted in Figure 6.7. The mean hydrodynamic radii are intensity averaged value over 10 min of measurement directly following 10 min temperature equilibrium for each temperature. It is evident that silica particles have a narrow polydispersity at low temperatures of 10 °C and 25 °C. This confirms the stability of KE-P10 silica particles in [C₄mim][BF₄] at these temperatures, and is consistent with the steady and oscillation shear rheology. However, with increasing temperature above 40 °C the silica particles become unstable in [C₄mim][BF₄] and aggregate, which is evident in the data as an increase in both the mean particle size and the width of the size distribution as indicated by the error bar. The DLS measurements of unstable aggregation at 40 °C and above directly confirm the loss of particle stability of KE-P10 silica particles in [C₄mim][BF₄] at high temperatures. Again, this is in good agreement with the rheological results.

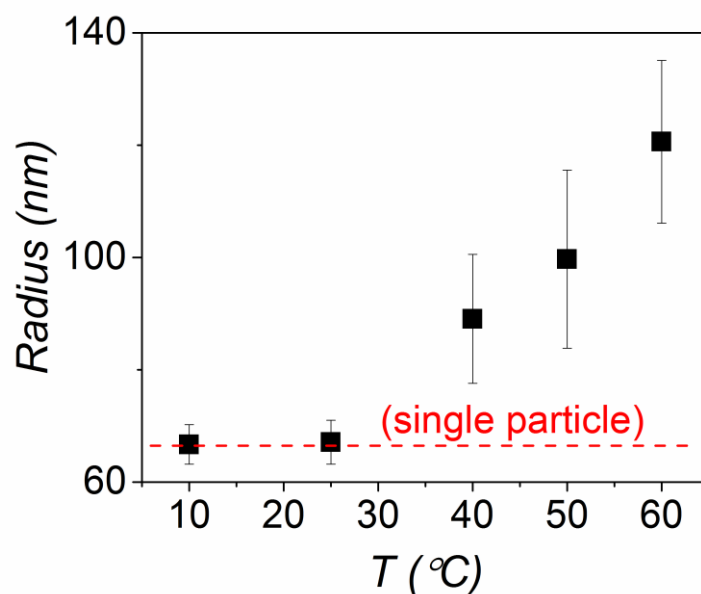


Figure 6.7: Hydrodynamic radius (intensity average) of KE-P10 silica particle or aggregations in $[C_4mim][BF_4]$ measured by DLS at the temperatures noted. Error bar is the standard deviation of measured particle size, indicating the polydispersity of particle or aggregations.

The solution structure measured by SANS is used to determine the inter-particle interaction in $[C_4mim][BF_4]$ at different temperatures. The scattering profiles of $\phi = 0.4$ KE-P10 silica particles in $[C_4mim][BF_4]$ at various temperatures are shown in Figure 6.8a. Scattering intensities at high q range ($> 10^{-2} \text{ \AA}^{-1}$) overlap for all the temperatures investigated as expected due to the essentially constant form factor of the silica particles at all temperatures. However, the intensities at low q ($< 10^{-2} \text{ \AA}^{-1}$) increase progressively with temperature. Intensities at low q are correlated to large scale structure in dispersion, hence an increase of intensity at low q indicates an increase in structure of the particle phase in $[C_4mim][BF_4]$.⁴¹ This structuring indicates stronger attraction at higher temperatures,⁴⁵ consistent with the previous

steady shear and small amplitude oscillation shear rheological results. In addition to hydrodynamic interactions and Brownian motion, the most important interparticle forces acting between silica particles in ILs are van der Waals attractions, electrostatic repulsion,¹⁷ and the solvation repulsive force.⁶ Electrostatic forces are negligible at all but the smallest separations due to the high ion concentration in ILs,^{6, 18, 49} so the dominated interparticle force between silica particles are van der Waals attraction and solvation layer repulsion. Model calculations of the DLVO potential between 100 nm silica particles in [C₄mim][BF₄] have been studied by Gao and Wagner.⁶ While electrostatic repulsion between silica particles in ILs can be neglected, the van der Waals attraction is always present. As the Hamaker constant of two silica particles in [C₄mim][BF₄] is relatively insensitive to temperature change, van der Waals attraction are expected to be nearly independent of temperature. Hence, the increase in strength of attraction with increasing temperature can be quantitatively linked to a reduction in the extent of stabilizing solvation layer on the particles.

The thickness of solvation layers around particle surface and strength of attraction between silica particle at different temperatures can be extracted from the SANS scattering intensities of silica particles in [C₄mim][BF₄] by fitted to a “sticky” hard sphere model in the form of a short range, square well potential. Using the same fitting method as for the sample at room temperature, which is shown in Figure 6.6b, the best fit solvation layer thickness and effective strength of attraction - stickiness parameter τ_b - are plotted as a function of temperature in Figure 6.8b. The stickiness parameter τ_b is inversely related to the strength of attraction between particles, such that the smaller the value, the stronger the interparticle attraction.⁵⁰⁻⁵² In the limit that $\tau_b \rightarrow$ infinity, hard sphere behavior is recovered, while sticky hard spheres have a

critical value for phase separation of $\tau_b = 0.11$. It is evident that τ_b decreases with increasing temperature, indicating much stronger attraction at higher temperatures, which is consistent with the increased scattering intensities at low q for high temperatures.

This enhanced attraction at high temperatures can be more quantitatively understood now from the measured thickness of solvation layers. As shown in Figure 6.8b, solvation layers of silica particles in $[\text{C}_4\text{mim}][\text{BF}_4]$ become thinner as temperature increases, such that the van der Waals attractions between particles will become more significant. Solvation layers are composed of anion and cation layers, which are initiated by hydrogen bonds between alcohol group on particle surface and anion group of $[\text{C}_4\text{mim}][\text{BF}_4]$. It is well known that hydrogen bonds are sensitive to temperature, especially to high temperature.⁵³⁻⁵⁴ The strength of such hydrogen bonds are expected to decrease significantly with temperature, *i.e.*, the strength and number of hydrogen bonds per water molecule are found to decrease as the temperature is increased.⁵³⁻⁵⁴ I find that the solvation layers surrounding these silica particles decrease slightly from 2.7 nm to 2.3 nm with increasing temperature from 10 °C to 25 °C. Model calculations of van der Waals forces⁶ suggest that the van der Waals attraction between two silica particles is nearly identical for these interparticle separation distances, which is twice the solvation layers thickness. This calculation is consistent with the steady shear and small amplitude oscillation shear rheology, which show that the change of rheological response simply arises from the viscosity change of the IL itself from 10 °C to 30 °C. However, van der Waals attractions increase dramatically when the minimum separation distance between two particles decreases as a result of the reduction in the solvation layers at higher temperatures. van der

Waals attraction is expected to dominate the interaction between particles at this reduced solvation layer thickness. As a result, silica particles lose stability and (reversibly) aggregate. The thinning of solvation layers and the loss of stability of silica particles results in a dramatic rise in the low shear viscosity for temperatures above 30 °C. This is the source of the significant higher TTS shift factor a_T than expected from the thermal viscosity of [C₄mim][BF₄] itself at 40 °C and above.

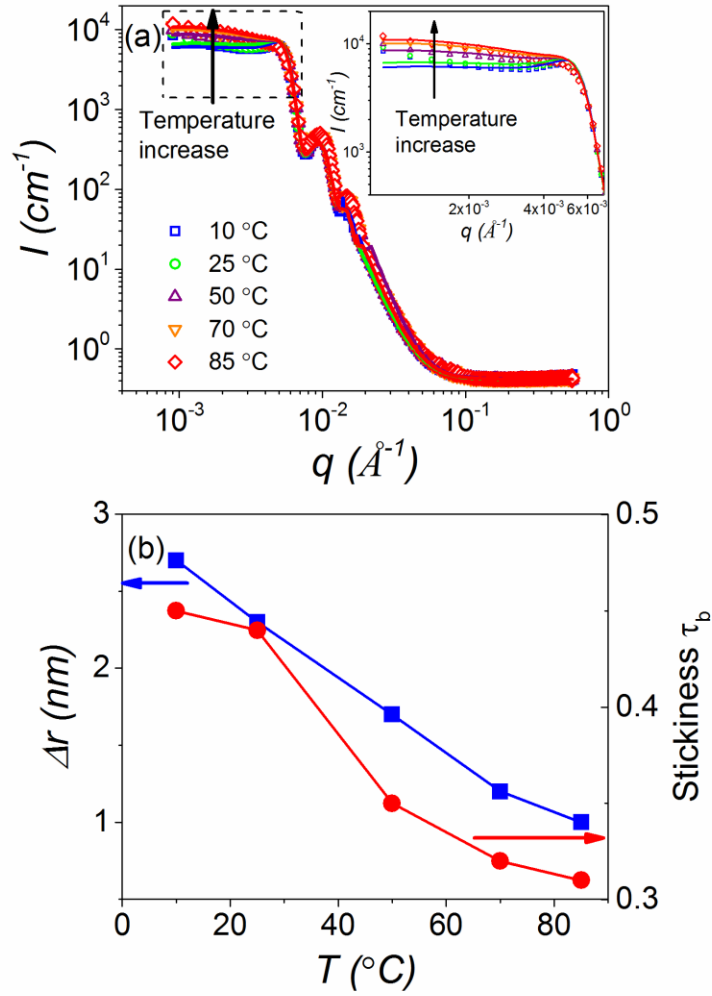


Figure 6.8: (a) SANS profiles of $\phi = 0.4$ silica particle – $[C_4mim][BF_4]$ dispersion at various temperatures with “sticky” hard sphere structure factor model fittings; (b) Extracted solvation layers thickness and stickiness parameter τ_b of different temperatures from SANS fitting of $\phi = 0.4$ silica particle – $[C_4mim][BF_4]$ dispersion.

From prior experimental and theoretical work, the liquid or gel state of dispersions also can be determined from the values of stickiness parameter τ_b , which

can be loosely interpreted as an inverse temperature or strength of attractions, and the universal adhesive hard-sphere (AHS) state diagram. The τ_b values for $\phi = 0.4$ KE-P10 silica particles in $[\text{C}_4\text{mim}][\text{BF}_4]$ at various temperatures extracted from the SANS fitting are plotted on the state diagram of AHS particles^{52, 55} and shown in Figure 6.9. With the decrease of τ_b , the attraction between AHS particles increases and the state of the dispersion transitions from a liquid state to a gel state. The dash line in the figure is the experimentally determined gel line for 100 nm diameter AHS particle dispersions.⁵⁵ As the size of KE-P10 particles is close to 100 nm, this gel line is used as a reference to determine the state of KE-P10 silica particles in $[\text{C}_4\text{mim}][\text{BF}_4]$. For the $\phi = 0.4$ KE-P10 silica particles dispersed in $[\text{C}_4\text{mim}][\text{BF}_4]$ at temperatures from 10 °C to 30 °C, the sample is predicted to be in a liquid state, in an agreement with experiments. From the SANS measurements, I anticipate that the dispersion will become a gel with increasing temperature, as observed. This liquid to gel state transition with increase of temperature is in a good agreement with rheological response of KE-P10 silica particles in $[\text{C}_4\text{mim}][\text{BF}_4]$.

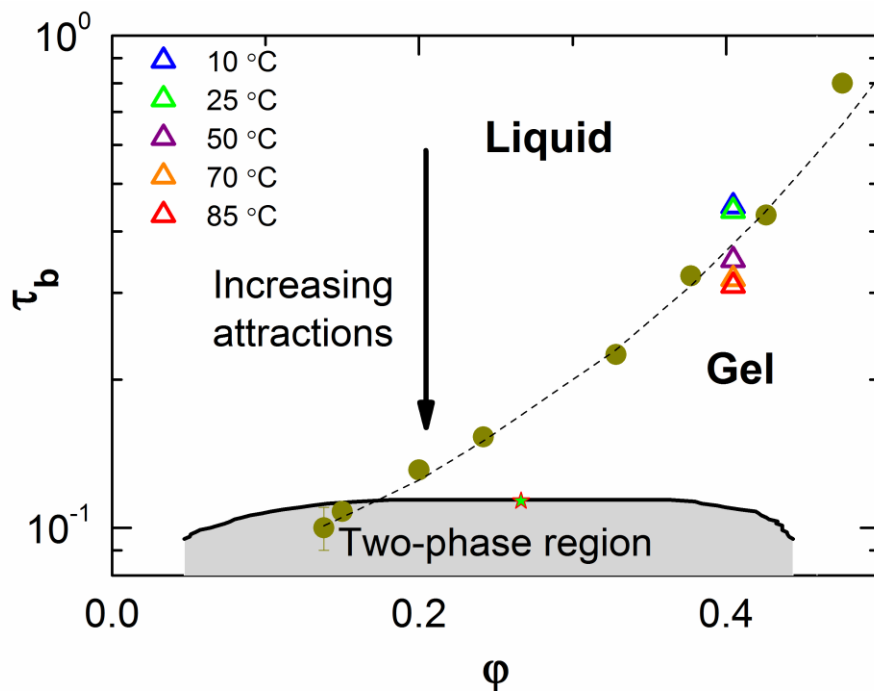


Figure 6.9: State positions of $\phi = 0.4$ silica particle – $[\text{C}_4\text{mim}][\text{BF}_4]$ dispersion at different temperatures in state diagram of AHS particle system.⁵² The dark-yellow circle points are the experimental gel points of particles of 100 nm diameter size⁵⁵ and a gel line shown as the dash line is determined from the experimental gel points.

6.4 Conclusions

In conclusion, I demonstrate that by tuning the strength of hydrogen bonds between particle surface and anions of ionic liquid, stable shear thickening colloidal dispersions can be formulated in ILs. At room temperature, this concentrated silica nanoparticle dispersion in $[\text{C}_4\text{mim}][\text{BF}_4]$ displays stronger shear thickening than the previous studied fluorocarbon coated silica particle system. It is shown that this is a consequence of the thinner solvation layers (~ 3 nm) initiated by relatively weaker hydrogen bonds between the hydrocarbon surface coating and anion group in comparison to the thicker solvation layers on the fluorinated particle surface, which

creates strong hydrogen bonds. This 3 nm solvation layers provides sufficient stabilization force between particles, while still allowing the particles to approach and shear-thicken at high shear rate/stress. This finding provides guidance for formulating stable, shear thickening dispersions in ILs.

Inverse melting is observed above 30 °C, indicating formation of gel. The mechanism driving increased particle attraction and loss of particle stability with increasing temperature is shown to be caused by a reduction in the solvation layer thickness, which itself is a result of the weakening of the hydrogen bonds with the surface at high temperatures. The horizontal shift factors a_T determined from TTS measurements confirm the increase of particle-particle attraction and loss of stability of colloidal dispersions above 30 °C. A transition from stable dispersion to unstable gel with increasing temperature also is independently confirmed by comparison with the established AHS particle state diagram. This state transition is in the opposite direction of traditional reported gel transition for coated particles dispersions at low temperatures, such as octadecyl coated silica suspended in *n*-tetradecane,^{52, 55} which is due to fundamentally different stabilization mechanisms. Nevertheless, the AHS state diagram provides a good reference for this new nanoparticle dispersion in IL. This novel gel transition at high temperatures, the investigation of the surface solvation structure and the corresponding interparticle potential provide a model study for material design through surface modification and temperature control. This basic principle is expected to be applicable to dispersions of many other functional colloidal particles, such as metals, magnetic and semiconductor particles in ILs.

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Chapter 7

PENETRATION RESISTANCE OF IONIC LIQUIDS BASED SHEAR THICKENING FLUIDS (STFS)-KEVLAR[®] NANOCOMPOSITES

The penetration resistance of ionic liquids based STFs- Kevlar[®] nanocomposites is described in this chapter. The effect of changing from the traditional STF carrier medium (PEG) to ionic liquid [C₄mim][BF₄] has been studied. Optimal areal density, penetration peak force, and dissipated energy are obtained through varying the treatment condition, such as the mixing ratio of ethanol to STFs. The resistance against threats from a spike and 21 & 18 gauge needles are evaluated for the ionic liquid based STF- Kevlar[®], and the results are compared with PEG-based STF- Kevlar[®].

7.1 Introduction

Traditional personal body armors are protective covering materials used to prevent an individual from being inflicted through direct contact with weapons, such as sharp instruments or projectiles from a potentially dangerous environment or action.¹⁻³ Recent trends have led to an increasing demand for stab protection.² Stab threats include direct attacks from knives and sharpened instruments, as well as physical contact with debris, broken glass, and razor wire.⁴ Thus, it is imperative to develop body armor systems with stab-resistant capabilities. There are two types of stab threats: puncture and cut. Puncture refers to penetration caused by instruments with sharp tips but no cutting edge, for example, ice picks or awls. Cut refers to contact with knives with a continuous cutting edge.

Numerous research efforts have been carried out to develop flexible, lightweight, and wearable soft body armor.^{2-3, 5} Previous studies have used high yarn count woven aramid fabrics, such as Kevlar[®] fabric from DuPont, impregnated with a colloidal, discontinuous shear thickening fluid (STF), and their protective properties including stab^{2, 5-6} and ballistic⁷⁻⁸ protection are evaluated. These investigations have shown that STF-fabric nanocomposite offers superior protective properties as compared to the neat fabrics, without compromising the weight and flexibility of the fabrics.

STFs can exhibit orders-of-magnitude increase in viscosity at high shear rate or shear stress,⁹⁻¹⁰ thus they have been intercalated with protective fabrics, such as Kevlar[®], to create enhanced protective materials often referred as STF-Armor[™]. STF-Armor[™] has been shown to provide superior protection against ballistic, and puncture threats. STFs behave like a liquid under rest that is flowable and low viscosity. However, when high shear rate or shear stress are applied, such as applying a strong impact, STFs turn into rigid with dramatic increase in viscosity and exhibit great energy dissipation capability. Thus, STFs can be used as an additive material to improve the performance of regular body armor made by Kevlar[®] fabric, allowing the flexibility of fabrics at normal movements while providing the armor with rigidity to resist threats from bullets, stabbing knife, and so on.

The mechanisms of how the addition of STF improves penetration resistance have been studied^{3-4, 6-8, 11-12} which includes dissipation of viscous energy within the STF itself, stress-coupling between adjacent fabrics, and a reduction in yarn mobility.² Decker et al.² performed quasi-static spike tests on STF-Kevlar[®] fabrics, showing that the addition of STF significantly improves the puncture resistance of Kevlar[®] fabrics.

The enhancement is attributed to a decreased yarn mobility within the fabric, which is consistent with prior yarn pull-out¹³⁻¹⁵ and ballistic tests.¹² The STF's act to restrict the relative motion of the fibers and yarns, which prevent the sharp tip of the spike from pushing aside yarns and fibers and penetrating between them. The reduction in the mobility of yarns also has been demonstrated to improve the energy absorption, which forces a probe to engage and ultimately break more yarns.¹¹ In addition, it has been proven that the enhancement of protective properties provided by STF addition is not limited to high speed impact events, but also occurs during quasi-static puncture tests. During quasi-static puncture, localized stress generated in the STF at the point of penetration exceeds the critical shear thickening stress, which can be transmitted to the surrounding fabric, i.e., shear thickening occurs immediately in a region surrounding the point of impact.² Thus, more surrounding fabrics are involved in the energy dissipation of puncture threats, resulting in enhanced protection property.

All the prior STF-fabric studies are focused on the STF's of particles dispersed in poly(ethylene glycol) (PEG). Recently, silica particles in ionic liquids (ILs) have been reported to display shear thickening behavior.¹⁶⁻¹⁸ Significant viscosity increase is observed at high shear rate for solid-spherical silica particles in the IL [C₄mim][BF₄] (more details are discussed in Chapter 6). Because of their vacuum stability property,¹⁹⁻²⁰ this ionic liquid based STF enables the use of STF-fabric soft body armor no longer limited to the application on earth, but also can be put into the extra-vehicular activity (EVA) suit to protect astronaut against threats from micrometeoroids and orbital debris (MMOD) particles.²¹⁻²²

In this chapter, Kevlar[®] fabrics are modified and treated with ionic liquid and its shear thickening fluids for the first time. I have investigated the performance of

stab resistance against spike puncture threats and needle cutting threats for the ionic liquid based STF-Kevlar[®]. The influence of ionic liquid itself on the penetration performance of Kevlar[®] fabric have been evaluated to ensure no lubricating or fiber damaging effect on Kevlar. The STF-Kevlar[®] treatment condition, such as the mixing ratio of ethanol to STFs, has been examined in terms of increased areal density, penetration peak force, and dissipated energy. Both of the spike and needle quasi-static penetration tests have been performed on the ionic liquids based STF-Kevlar[®] and the results are compared with traditional PEG-based STF-Kevlar[®].

7.2 Materials and Methods

7.2.1 Materials

The IL [C₄mim][BF₄] (>99% pure) was purchased from Iolitec to prepare silica particle dispersions. The poly(ethylene glycol) (M_w = 200, PEG-200) was obtained from Clariant. Two different sizes of silica nanoparticles KEP10 (radius a = 60 nm) and KEP50 (radius a = 260 nm) were purchased from Nippon Shokubai Co. (Tokyo, Japan) and were used to treat the Kevlar[®] fabric directly or to prepare concentrated silica particle - ionic liquid [C₄mim][BF₄] suspensions displaying shear thickening behavior. At 50 vol%, the STF sample exhibits extreme shear thickening behavior. More details about the preparation and rheological behavior of shear thickening fluids can be found in Chapter 6.

Protective Kevlar[®] 1148 fabric (untreated or treated with PEG based STF) was purchased from Barrday Inc. (Cambridge, Ontario, Canada). The areal density for untreated Kevlar[®] 1148 and treated STF- Kevlar[®] 1148 are 159 g/m² and 183 g/m², respectively. In the lab, in order to intercalate silica particle or STFs into the fabric,

the silica particles or STFs were diluted with ethanol at certain volume ratio to obtain a homogenous mixture. In this chapter, the effect of the mixing volume ratio of ethanol to silica particle/STF (e.g. 1:1, 2:1, 3:1 and 4:1) on the penetration resistance of Kevlar[®] fabric is discussed. Each individual Kevlar[®] 1148 fabric sheet (3 inch $\times$ 3 inch) was soaked into the mixture for 1 min before being squeezed through rubber-coated nip rollers to remove extra ethanol/STF mixture. Then each treated fabric sheet was hung to dry at room temperature for 5 min before dried in an oven for 1 h at 70 °C to remove the ethanol. All the fabrics including solvent treated, dry silica particle treated, and STFs treated, were dry to the touch. Fabrics that were solvent treated or STFs treated have a uniform appearance; however, the dry silica particle treated fabrics appear whitened streaky. The silica particles on the fabric can be easily peeled off when contacting with surface, leaving a white residue of dry particles. In contrast, for solvents or STFs treated fabrics, there was no obvious residue left on the contact surfaces.

Eight different fabric treatments were studied and compared in this chapter: untreated, ethanol, PEG-200, ionic liquid [C₄mim][BF₄], dry silica particle, $\phi = 0.5$ KEP50 in PEG 200, $\phi = 0.6$ KEP50 in ionic liquid [C₄mim][BF₄], and $\phi = 0.5$ KEP10 in ionic liquid [C₄mim][BF₄]. The mass or volume addition of each coating to the fabric can be controlled by tailoring the dilution ratio of treatment materials to ethanol in the soak bath. It is reported that sub-micro particles intercalate between fibers and yarns in the void space of the woven fabric.^{7, 12, 23-24} In order to have a reasonably consistent geometric packing and filling of the particles in the fabrics, the volume fraction of added particles needs to be controlled. Thus, when the fabric is treated with dry silica particles, the dilution with ethanol is twice as much so as to have

comparable particle concentrations in the coating fluid, for example, the dilution ratio of ethanol to dry particle is 2:1 in comparison to the 1:1 dilution for the STF treated fabrics.

7.2.2 Quasi-Static Puncture Tests

The puncture resistance of the Kevlar[®] fabrics with or without STFs treatments were evaluated by quasi-static puncture test. During the measurement, the ASTM F-1342 standard was followed.²⁵ An A0 6-1/4" awl spike from Malco Products, Inc. was used to simulate the threat from sharp objects without cutting edge. Two different gauges of hypodermic needles with standard bevel tips: 18G (1.270 mm outer barrel diameter), and 21 G (0.800 outer barrel diameter) were used to simulate the threat from sharp-cutting edge objects (referred to Chapter 2 Figure 2.10 for more details). Between each experiment, the needle is replaced by a fresh one to ensure the same sharpness.⁶ The spike or needle was held within the chunk that was mounted to a 500 N load cell on an Instron 5965 instrument. One single layer of Kevlar[®] fabric was used for the spike puncture tests and 4-layer assemble of Kevlar[®] fabric was used for needle penetration tests. The spike or needle was loaded at a constant quasi-static speed of 10 mm/s approaching to the fabrics. Zero displacement and zero force were defined when the probe nearly touched the fabric. The force experienced by the probe was recorded as a function of displacement. Twelve replicates were conducted on each sample at different spots to obtain a meaningful statistical value. The force resistance of the tested fabrics is evaluated by the maximum value of the force in the force-displacement curve, which is considered as the penetration peak force, and the dissipated energy until the penetration of fabric. The dissipated energy is the integral of force vs. displacement (the area underneath the force vs. displacement curve) until

reaching the penetration peak force. Combined with the areal density (weight/area) of Kevlar[®] fabric, those three factors are considered when designing the lightweight soft body armor materials.

7.3 Results and Discussion

7.3.1 Spike Penetration Measurements

7.3.1.1 Effect of STFs Carrier Medium

It has been known that ionic liquids have a lubricating effect when applied to the surface of various materials,²⁶⁻²⁹ especially under vacuum condition,²⁸⁻²⁹ such that, it can be used as a lubricant with broad applications. Due to the lubricating effect of ionic liquids, the penetration resistance of Kevlar[®] fabric treated by ionic liquids based STFs may be reduced due to increased mobility of yarns with the present of ionic liquid. Moreover, ionic liquids have shown an ability to dissolve a great variety of materials including various polymers.^{19, 30} They have the potential to dissolve and damage Kevlar[®] polymer fiber, which would result in a reduction in the puncture force resistance for Kevlar[®] treated by ionic liquid based STFs. Due to these properties of ionic liquids, the lubricating and dissolving effect of ionic liquids on Kevlar[®] fabric need to do examined.

Kevlar[®] 1148 fabrics (3 inch × 3 inch, 12 pieces) were treated by ethanol, ionic liquid [C₄mim][BF₄], and PEG 200, and their puncture resistance against spike were evaluated. Their increased areal density after treatments are plotted in Figure 7.1 and compared in Table 7.1. As the ethanol evaporates from the fabrics during drying in the oven, there is nearly no density increase as shown in the Figure 7.1. The uptake of IL [C₄mim][BF₄] by Kevlar[®] is larger in comparison to PEG 200, resulting in doubled

increment of areal density than the PEG 200 treated Kevlar[®]. The force curves (12 replicates) punctured by spike for one layer Kevlar[®] fabric with and without solvents treatments are shown in Figure 7.2. The variability of force curves of twelve replicates for each treatment is due to the woven nature of the Kevlar[®] fabric. For each of the Kevlar[®] samples, including the untreated one, the results of twelve replicates can be divided to two groups: low penetration peak force and high penetration peak force. The low penetration peak force for each particular treatment condition occurs when the spike contacts the interstitial area between yarns during puncture, resulting in the penetration mainly due to “windowing” of fabric, that is, the spike penetrates through an open area by spreading apart yarns.¹⁻² In contrast, when the spike contacts at the cross-over area of yarns, fibers fracture with “windowing” occurred during the penetration, resulting in the high penetration peak force.

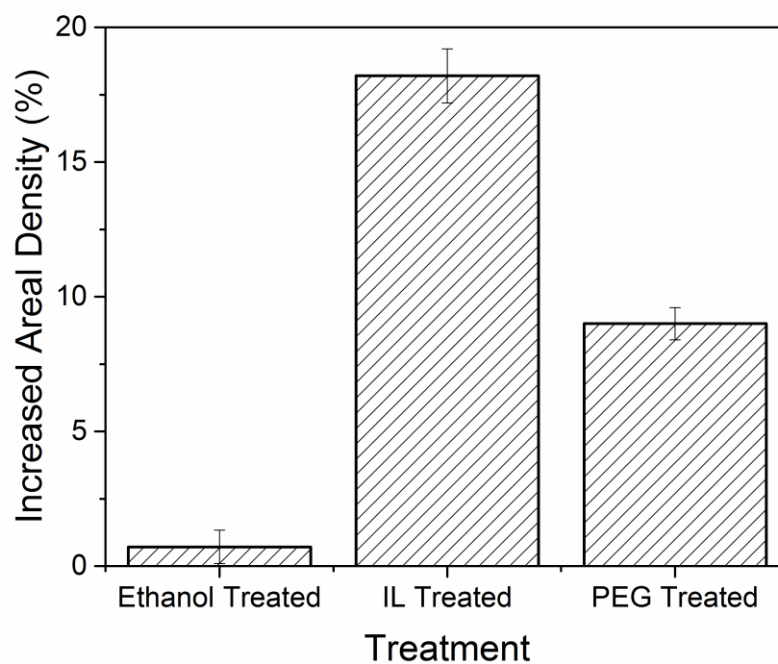


Figure 7.1: The increased areal density (%) of Kevlar[®] 1148 fabric (3 inch × 3 inch) after treated by various solvents: ethanol, ionic liquid ([C₄mim][BF₄]), and PEG 200.

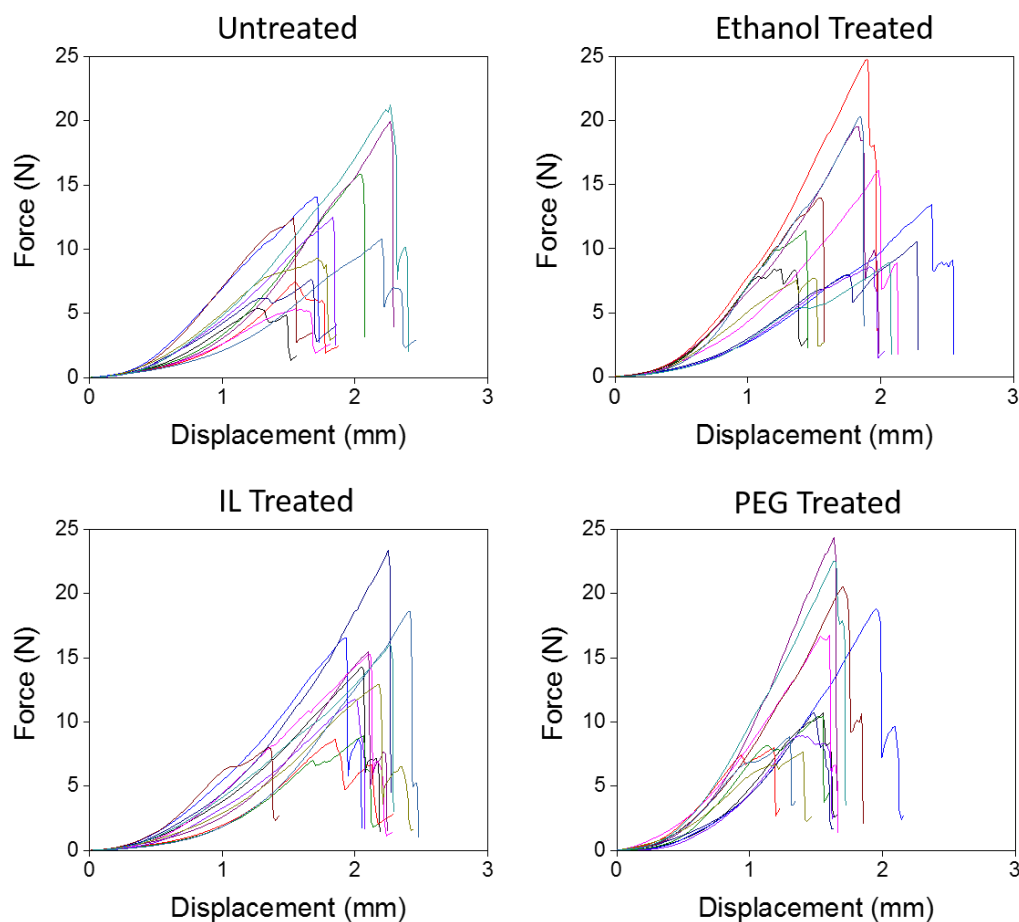


Figure 7.2: The force curves (force vs. displacement) of Kevlar[®] 1148 before and after treated by solvents: ethanol, ionic liquid ($[C_4mim][BF_4]$), and PEG 200 with twelve repeats.

The penetration peak force and dissipated energy for each treatment are shown as box chart in Figure 7.3. Table 7.1 summaries the statistical value of penetration peak force and dissipated energy. It can be observed that, after treatments with different solvents: ethanol, ionic liquid, or PEG 200, the penetrate peak force and the dissipated energy of Kevlar[®] 1148 during puncture tests are similar to the untreated fabric. A t-test is performed between each treatment and untreated one, and their p-

values are listed in Table 7.1. At 95% confidence, it is obvious that there is no significant difference in the penetration peak force and dissipated energy between untreated Kevlar[®] and solvent treated Kevlar[®]. Thus, it is evident that ionic liquids have no significant lubricating or dissolving effect on the Kevlar[®] fabric; thus, the puncture resistance is not adversely affected when the fabric is treated with ionic liquids.

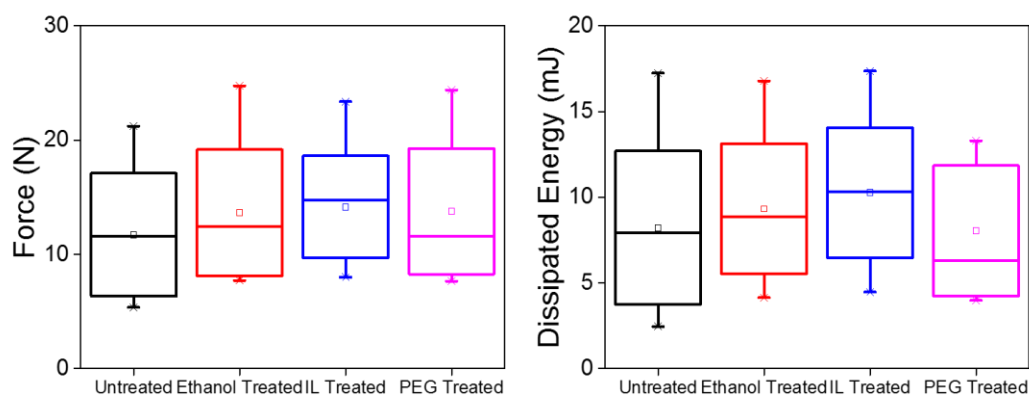


Figure 7.3: Box charts of penetration peak forces and dissipated energies for Kevlar[®] 1148 with or without solvents treatments.

Table 7.1: Summary of increased areal density (%), penetration peak force with its p-value of t-test (two-sample t-test compared with untreated Kevlar[®] 1148), and dissipated energy with its p-value of t-test (two-sample t-test compared with untreated Kevlar[®] 1148) for Kevlar[®] 1148 before and after treatment by solvents: ethanol, ionic liquid ([C₄mim][BF₄]), and PEG 200.

Treatment	Untreated	Ethanol Treated	IL Treated	PEG 200 Treated
Increased Areal Density (%)	---	0.71 ± 0.62	18.2 ± 1.00	9.00 ± 0.60
Peak Force (N)	11.71 ± 5.38	13.64 ± 5.51	14.14 ± 4.47	13.77 ± 5.51
p-value (t-test)	---	0.39	0.24	0.36
Dissipated Energy (mJ)	8.22 ± 4.48	9.32 ± 3.79	10.27 ± 3.80	8.03 ± 3.81
p-value (t-test)	---	0.52	0.24	0.92

7.3.1.2 Effect of Ethanol: STF's Solution Ratio

STFs are mixed with ethanol to reduce the surface energy and viscosity of suspensions before treating the Kevlar[®] fabric. The effect of changing the mixing volume ratio of ethanol to STF's suspensions on puncture resistance is investigated. Kevlar[®] 1148 fabrics are treated by dry KEP50 silica particle, $\phi = 0.5$ KEP50-PEG STF, $\phi = 0.6$ KEP50-IL STF, and $\phi = 0.5$ KEP10-PEG STF. The increased areal densities (%) after treatments with four different mixing volume ratios of ethanol to STF's are shown in Figure 7.4. As expected, the increment of the areal density decreases with higher ethanol content due to the highly diluted STF concentration. However, the reduction in increased areal density is not significant when the mixing ratio changes from 3:1 to 4:1. For the same mixing ratio, Kevlar[®] 1148 treated by dry KEP50 silica particle has the lowest increase in weight due to the lack of non-evaporated solvents (such as ionic liquids or PEG). Dry silica particles are easily peeled off from the surface of fabrics without the adhesive effect of ionic liquids or PEG. Kevlar[®] treated by ionic liquid based STF's have slightly higher increased areal density than those treated by PEG based STF with the same particle concentration.

Due to the higher particle concentration of STFs, there is more weight gain for Kevlar[®] treated with $\phi = 0.6$ KEP50 in ionic liquid than those with lower particle concentration of $\phi = 0.5$.

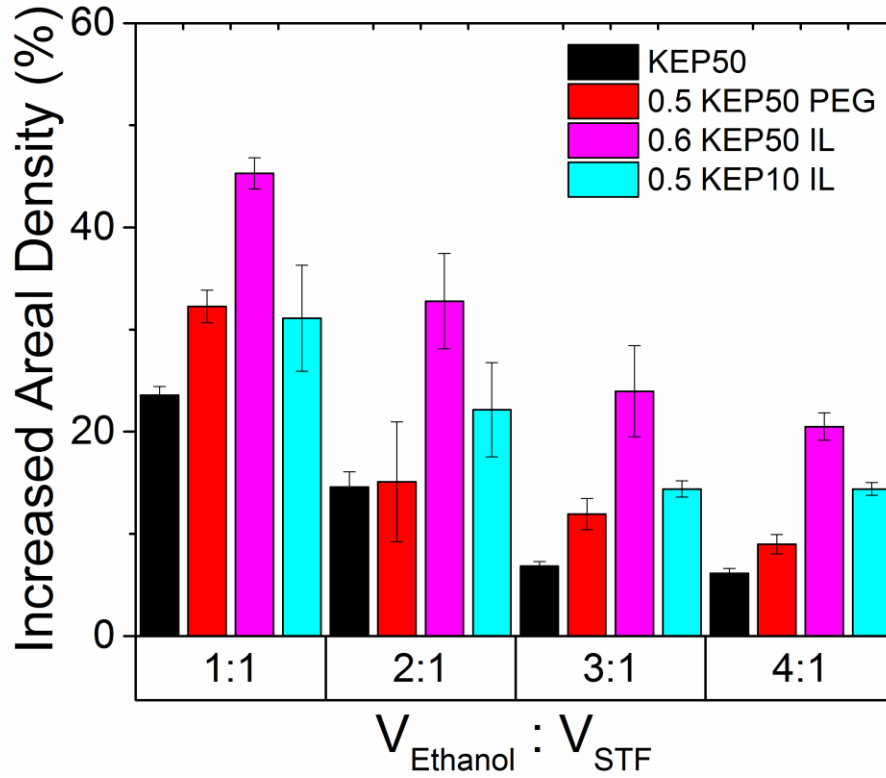


Figure 7.4: The increased areal density (%) of Kevlar[®] 1148 fabric (3 inch × 3 inch) after treated by dry KEP50 particle powder, and different STFs ($\phi = 0.5$ KEP50 in PEG 200, $\phi = 0.6$ KEP50 in ionic liquid [C₄mim][BF₄], and $\phi = 0.5$ KEP10 in ionic liquid [C₄mim][BF₄]) with different volume ratios of ethanol : treating materials (particles or STFs).

Spike penetration test is performed on one layer of the untreated and treated Kevlar[®] fabrics. The penetration peak forces and dissipated energies of Kevlar[®] treated by dry KEP50 silica particles are shown as chart box in Figure 7.5, and their statistical values are listed in Table 7.2. It is evident that Kevlar[®] treated by dry silica particles possesses higher penetration resistance with higher penetration peak force and higher dissipate energy than untreated fabric. This observation is consistent with previous findings by other researchers.^{2, 7-8} When comparing the penetration resistance performance for different mixing ratios of ethanol to dry particle, the penetration peak force and dissipated energy for ratio condition of 2:1 and 3:1 are comparable and significant higher than those of 1:1 and 4:1. For more condensed mixture with the ratio of 1:1, the mixture looks like a slurry which might result in an unevenly treated Kevlar[®] surface leaving certain surface untreated. The penetration resistance performance would be lower at the untreated surface. However, for the most dilute mixture of 4:1 ratio, the low silica particle content in between the yarns causes insufficient yarn matrix connection to dissipate energy, which leads to a lower penetration resistance performance. Thus, when treated the fabrics with ethanol to dry particle ratio equal to 2:1 and 3:1, the penetration resistance performance of Kevlar[®] is optimal.

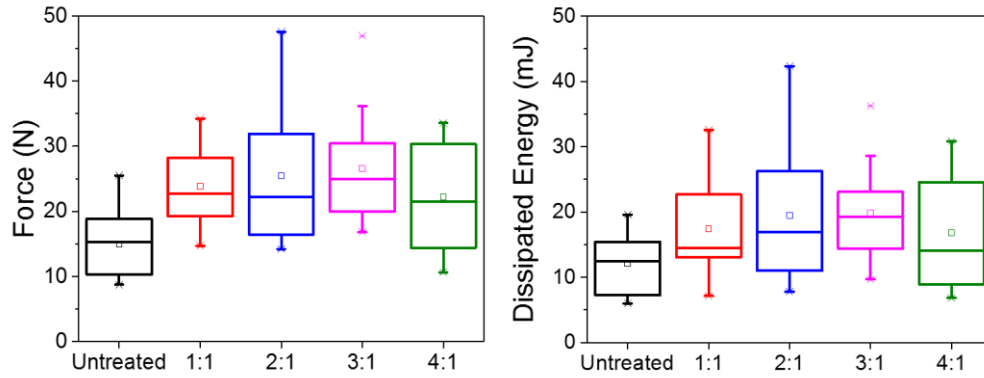


Figure 7.5: Box charts of penetration peak forces and dissipated energies during spike penetration measurements for Kevlar[®] 1148 before and after treated by dry KEP50 particle powders with various volume ratios of ethanol : KEP50.

Table 7.2: Summary of increased areal density (%), penetration peak forces, and dissipated energies during spike penetration measurements for Kevlar[®] 1148 before and after treatment by dry KEP50 particle powders with various volume ratios of ethanol : KEP50.

	Untreated	$V_{\text{ethanol}} : V_{\text{KEP50}}$			
		1:1	2:1	3:1	4:1
Increased Areal Density (%)	---	23.59 ± 0.83	14.57 ± 1.50	6.86 ± 0.43	6.15 ± 0.46
Peak Force (N)	14.94 ± 5.25	23.82 ± 6.17	25.41 ± 10.88	25.54 ± 8.78	22.18 ± 8.38
Dissipated Energy (mJ)	12.09 ± 4.89	17.40 ± 7.93	19.49 ± 10.70	19.87 ± 7.40	16.81 ± 8.78

Similarly, the penetration peak force and dissipated energy of Kevlar[®] treated by $\phi = 0.5$ KEP50 in PEG 200 with varying ethanol to STFs volume ratios are shown in Figure 7.6 and their statistical value are listed in Table 7.3. The penetration peak forces with the treatment mixing condition at 1:1, 2:1 and 3:1 are significant higher than that treated at condition of 4:1, while the dissipated energy are comparable for all the conditions. The penetration resistance results of Kevlar[®] treated by $\phi = 0.6$ KEP50

in ionic liquid are shown in Figure 7.7 and Table 7.4. When the volume ratio of ethanol to STF is equal to 3:1, both the penetration peak force and dissipated energy reach the maximum. For the Kevlar[®] treated by $\phi = 0.5$ KEP10 in ionic liquid (Figure 7.8 and Table 7.5), the peak force and dissipated energy of treated fabric at the ratio of 3:1 is slightly lower than that at condition ratio of 1:1. However, considering the areal density gain is more than doubled for the condition of 1:1 than that of 3:1 shown in Table 7.5, condition of 3:1 would be the optimal condition for the purpose of light-weight fabric protection.

In all cases, STF or particle intercalation improves the penetration force resistance and the energy dissipation capability of Kevlar[®] fabric, which are consistent with previous work suggesting improved puncture resistance with STF-treatments. Based on previous discussion, the ethanol: STF/dry particle volume ratio = 3:1 is the optimal condition to achieve the best puncture protection without compromising the weight of the Kevlar[®] fabric. For the higher STF/particle content (volume ratio of ethanol: STF = 1:1 or 2:1), the increased weight of fabrics is significant higher, which is not ideal for light-weight protection purpose. What is more, uneven treated fabric is intended to happen at the high STF content. For the lower STF/particle content case (volume ratio of ethanol: STF = 4:1), the small amount of STF or particle content in between yarns would not be able to sufficiently reduce the mobility of yarns and provide enough puncture resistance.

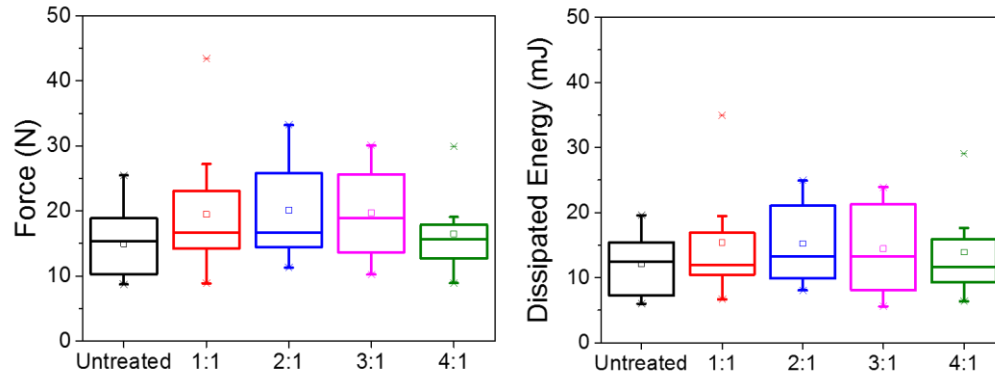


Figure 7.6: Box charts of penetration peak forces and dissipated energies during spike penetration measurements for Kevlar[®] 1148 before and after treated by STFs of $\phi = 0.5$ KEP50 in PEG 200 with various volume ratios of ethanol : STFs.

Table 7.3: Summary of increased areal density (%), penetration peak forces, and dissipated energies during spike penetration measurements of Kevlar[®] 1148 before and after treatment by STFs of $\phi = 0.5$ KEP50 in PEG 200 various volume ratios of ethanol : STFs.

	Untreated	$V_{\text{ethanol}} : V_{\text{STFs}}$			
		1:1	2:1	3:1	4:1
Increased Areal Density (%)	---	32.26 ± 1.60	15.08 ± 5.87	11.93 ± 1.52	8.98 ± 0.95
Peak Force (N)	14.94 ± 5.25	19.47 ± 9.10	20.09 ± 7.92	19.71 ± 6.92	16.48 ± 6.19
Dissipated Energy (mJ)	12.09 ± 4.89	15.42 ± 9.19	15.24 ± 6.29	14.45 ± 6.93	13.92 ± 7.11

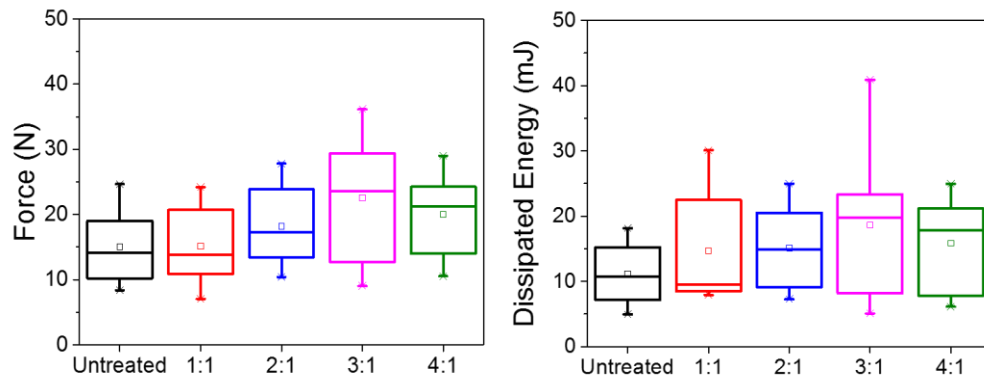


Figure 7.7: Box charts of penetration peak forces and dissipated energies during spike penetration measurements for Kevlar[®] 1148 before and after treated by STFs of $\phi = 0.6$ KEP50 in ionic liquid $[\text{C}_4\text{mim}][\text{BF}_4]$ with various volume ratios of ethanol : STFs.

Table 7.4: Summary of increased areal density (%), penetration peak forces, and dissipated energies during spike penetration measurements for Kevlar[®] 1148 before and after treatment by STFs of $\phi = 0.6$ KEP50 in ionic liquid $[\text{C}_4\text{mim}][\text{BF}_4]$ with various volume ratios of ethanol : STFs.

	Untreated	$V_{\text{ethanol}} : V_{\text{STFs}}$			
		1:1	2:1	3:1	4:1
Increased Areal Density (%)	---	45.29 ± 1.53	32.78 ± 4.67	23.97 ± 4.48	20.50 ± 1.35
Peak Force (N)	15.00 ± 5.37	15.11 ± 5.81	18.19 ± 6.00	22.58 ± 9.14	20.03 ± 6.29
Dissipated Energy (mJ)	11.13 ± 4.56	14.68 ± 8.26	15.11 ± 6.53	18.63 ± 10.46	15.84 ± 7.14

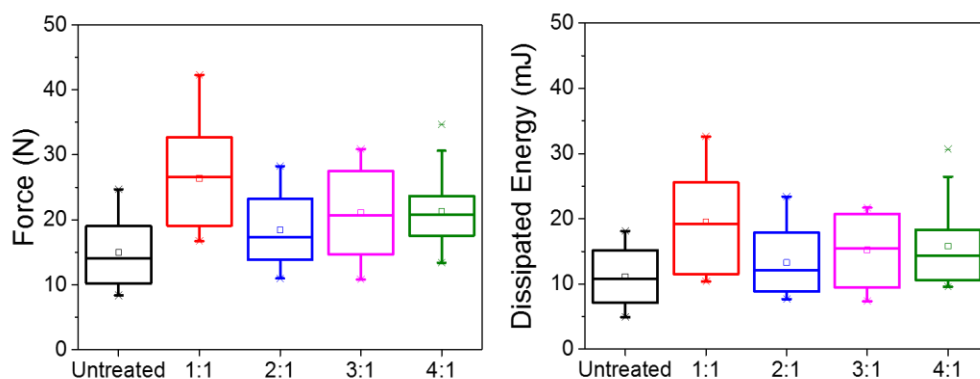


Figure 7.8: Box charts of penetration peak forces and dissipated energies during spike penetration measurements for Kevlar[®] 1148 before and after treated by STFs of $\phi = 0.5$ KEP10 in ionic liquid $[\text{C}_4\text{mim}][\text{BF}_4]$ with various volume ratios of ethanol : STFs.

Table 7.5: Summary of increased areal density (%), penetration peak forces, and dissipated energies during spike penetration measurements for Kevlar[®] 1148 before and after treatment by STFs of $\phi = 0.5$ KEP10 in ionic liquid $[\text{C}_4\text{mim}][\text{BF}_4]$ with various volume ratios of ethanol : STFs.

	Untreated	$V_{\text{ethanol}} : V_{\text{STFs}}$			
		1:1	2:1	3:1	4:1
Increased Areal Density (%)	---	31.11 ± 5.21	22.15 ± 4.61	14.40 ± 0.81	14.38 ± 0.63
Peak Force (N)	15.00 ± 5.37	26.39 ± 8.00	18.44 ± 6.00	23.38 ± 7.27	21.31 ± 6.32
Dissipated Energy (mJ)	11.13 ± 4.56	19.48 ± 8.17	13.29 ± 5.20	17.24 ± 5.77	15.81 ± 6.75

The puncture resistance properties of untreated and STF treated Kevlar[®] 1148 at the same treatment condition of ethanol: STFs volume ratio = 3:1 are listed in Table 7.6 and the results are compared with commercial STF-Kevlar[®] 1148 product from Barrday. The STF-Kevlar[®] 1148 (Barrday) has similar areal density and comparable dissipated energy capability as the ones prepared in lab; however, the former shows a

higher penetration peak force. This difference may come from different treatment protocols used as well as different STF formulations. For all the Kevlar[®] treated at lab scale, dry silica particle treated Kevlar[®] also shows a good penetration force resistance because the friction between particle and fabric reduces the mobility of the yarns. However, the yarns are more easily worn out due to the friction of dry particles, and the dry particles are easily peeled off from the fabric. For the wet-silica-Kevlar[®] treatments (STFs-Kevlar[®]), fabrics with the treatment of ionic liquid based STFs are proved to have good puncture resistance, which is even better than the one treated by PEG based STFs, making it promising to replace traditional PEG based STF-Kevlar[®] to use in space environment.

Table 7.6: Summary of increased areal density (%), penetration peak forces, and dissipated energies during spike penetration measurements for Kevlar[®] 1148 before and after treatments.

Treatment	Increased Areal Density (%)	Peak Force (N)	Dissipated Energy (mJ)
Untreated	---	15.00 ± 5.37	11.13 ± 4.56
Dry KEP50	6.86 ± 0.43	25.54 ± 8.78	19.87 ± 7.40
0.5 KEP50-PEG	11.93 ± 1.52	19.71 ± 6.92	14.45 ± 6.93
0.6 KEP50-IL	23.97 ± 4.48	22.58 ± 9.14	18.63 ± 10.46
0.5 KEP10-IL	14.40 ± 0.81	23.38 ± 7.27	17.24 ± 5.77
STFs (Barrday)	14.62 ± 2.24	31.12 ± 8.04	17.41 ± 7.95

7.3.2 Needle Penetration Measurements

The penetration resistance of Kevlar[®] treated by various STFs (identical ethanol: STFs volume ratio = 3:1) is also evaluated by hypodermic needle penetration

test. The penetration force curves of 4-layers Kevlar[®] fabrics with and without various STFs treatments using 18G and 21G gauge needles are shown in Figure 7.9 and Figure 7.10, respectively. The shape of the force-displacement curves is statistical in nature.³¹⁻³² Twelve replicates are performed for each treatment to get meaningful statistical results. The averaged force values at each displacement are shown in Figure 7.11.

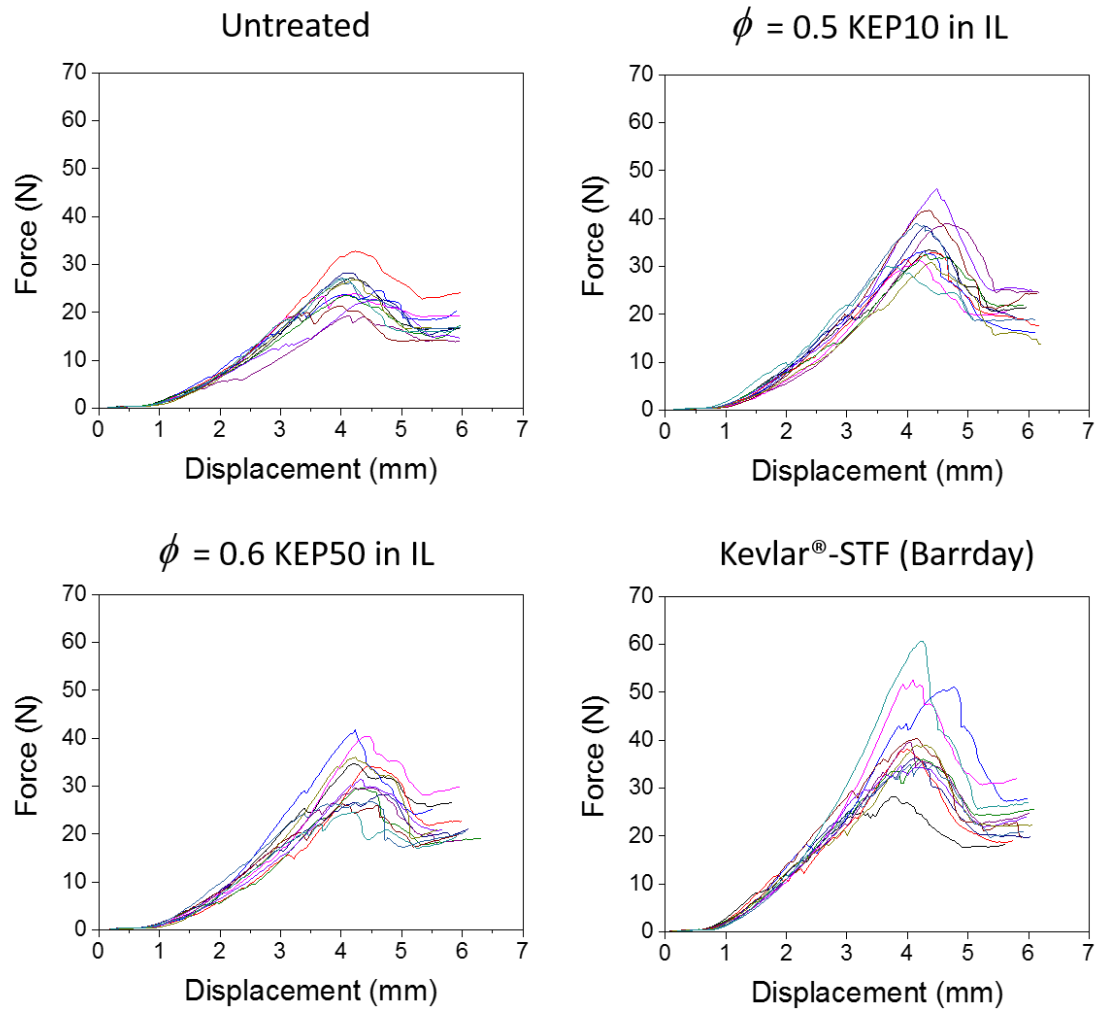


Figure 7.9: The force curves (force vs. displacement) of Kevlar[®] 1148 before and after treated with various STFs punctured by 18G needles with twelve repeats.

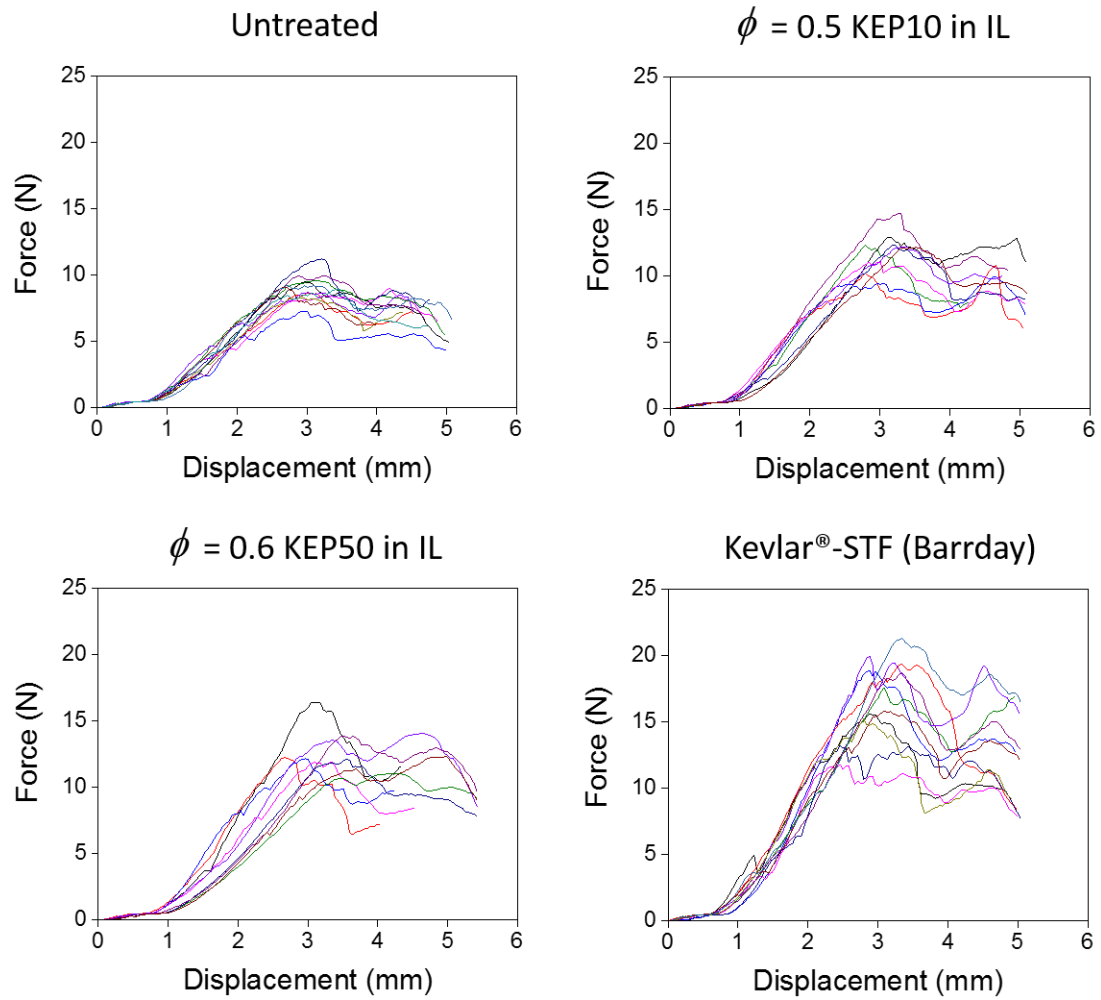


Figure 7.10: The force curves (force vs. displacement) of Kevlar[®] 1148 before and after treated with various STFs punctured by 21G needles with twelve repeats.

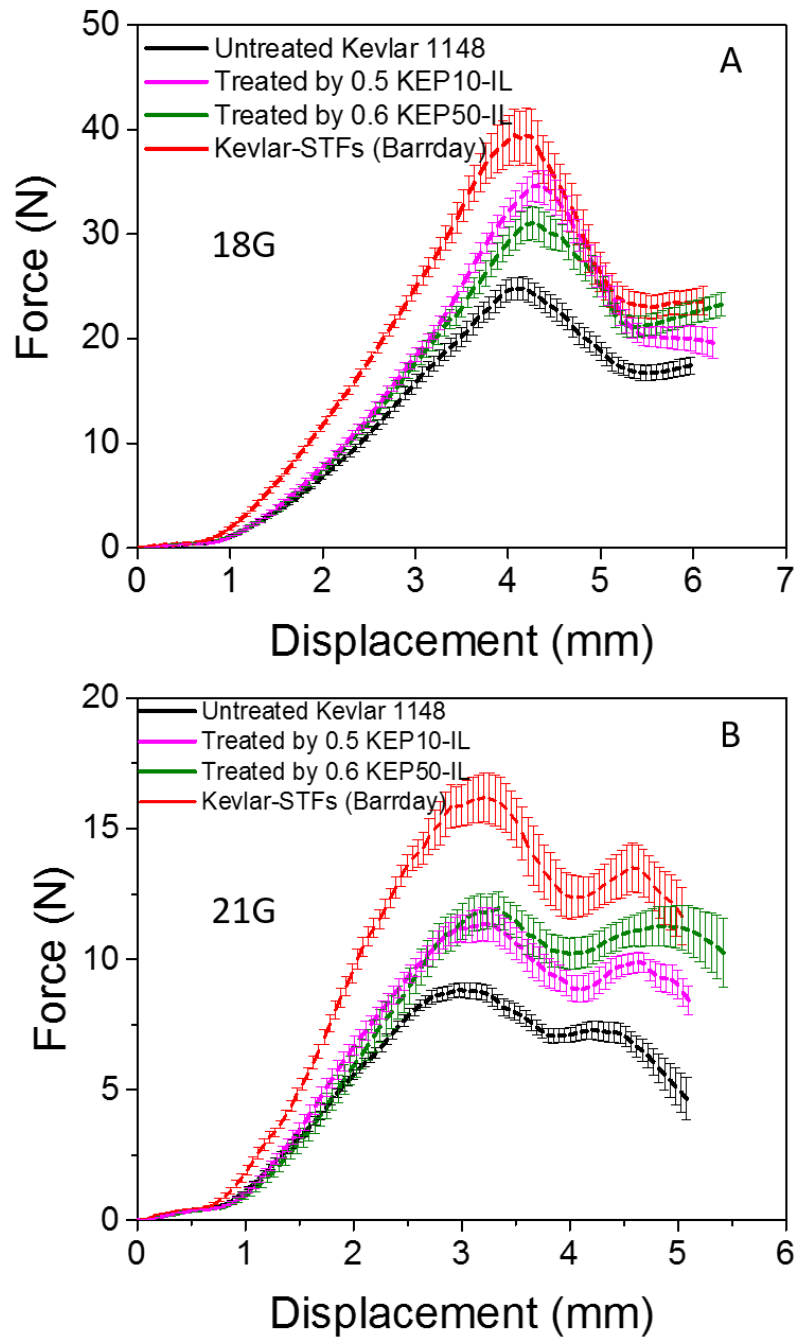


Figure 7.11: The averaged force curves (force vs. displacement) of Kevlar[®] 1148 before and after treated with various STFs punctured by needles of 18G (A) and 21G (B) with twelve repeats.

The average penetration peak force and dissipated energy of the Kevlar[®] fabrics during penetration process are measured to evaluate their penetration resistant capability, and the results are shown in Figure 7.12 and Figure 7.13, respectively. The statistical values of penetration resistance against 18G and 21G needles for each fabric treatment are reported in Table 7.7 and Table 7.8, respectively. For both of the 18G and 21G needle penetration threats, Kevlar[®] fabrics layers intercalated with STFs tend to have larger penetration peak force and higher dissipated energy than untreated Kevlar[®] fabric layers. This increase in penetration resistance is expected and consistent with previous research.^{2, 6, 22, 31}

Under the 18G needle penetration threats, Kevlar[®] fabrics treated by $\phi = 0.5$ KEP10 in ionic liquid have comparable penetration peak force as those of STF-Kevlar[®] (Barrday) with similar areal density, while the dissipated energy is lower than the STF-Kevlar[®] (Barrday). In contrast, after treated by $\phi = 0.6$ KEP50 in ionic liquid STF, Kevlar[®] fabrics have much higher areal density, while the penetration peak force and energy dissipated during the needle penetration are much lower than the STF-Kevlar[®] (Barrday).

For the quasi-static penetration test of smaller needle size 21G, the overall peak force and dissipated energy during penetration are significant lower than those using needle size of 18G. This reduced peak force and dissipated energy are the results of smaller contact surface area which favors occurrence of “windowing” of fabrics, i.e., needle penetrating through an open area by spreading apart of yarns.⁶ With the treatments of ionic liquid based STFs, Kevlar[®] fabrics display significant lower penetration peak force while having comparable energy dissipation capability as for PEG based STF-Kevlar[®] (Barrday).

From the previous discussions on both the 18G and 21G needle penetration tests, it is apparent that the penetration peak force and dissipated energy are decoupled, that is, high penetration peak force is not necessarily coupled with high energy dissipation capability. The dissipated energy is the integral of force vs. displacement (the area underneath the force vs. displacement curve). For Kevlar[®] fabrics that are able to involve more adjacent yarns to dissipate the energy, their penetration would be delayed to even larger displacement deformation before being penetrated. Thus, a higher energy dissipation capability can be obtained.

Kevlar[®] fabrics layers intercalated with ionic liquid based STF have significant enhanced penetration resistance than the untreated Kevlar[®] fabric layers during the needle penetration process. This enhanced needle penetration resistance allows the use of ionic liquid based STF-Kevlar[®] to provide better protection against cut hazards without compromising the weight and flexibility. Compared with the PEG based STF-Kevlar[®] nanocomposites, the ionic liquid based STF-Kevlar[®] nanocomposites show comparable but slightly lower protection capability against needle cutting threats. Similar to the spike puncture test cases, this lower needle penetration resistance phenomenon is coming from the difference in the treating process between the lab-scale and industrial-scale. However, it is promising that ionic liquid based STF-Kevlar[®] nanocomposite will have the same needle penetration resistance as the PEG based STF-Kevlar[®] when using the same treatment process.

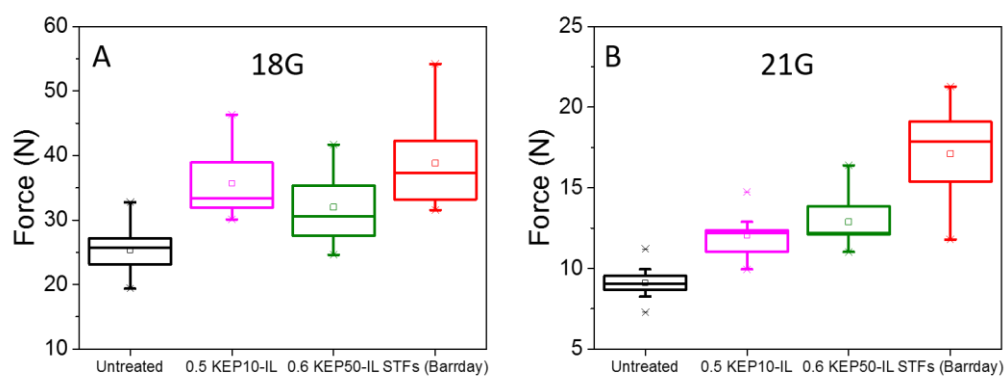


Figure 7.12: Box charts of penetration peak forces during 18G (A) and 21G (B) needle penetration tests for Kevlar® 1148 before and after treated by various ionic liquid based and PEG based STFs.

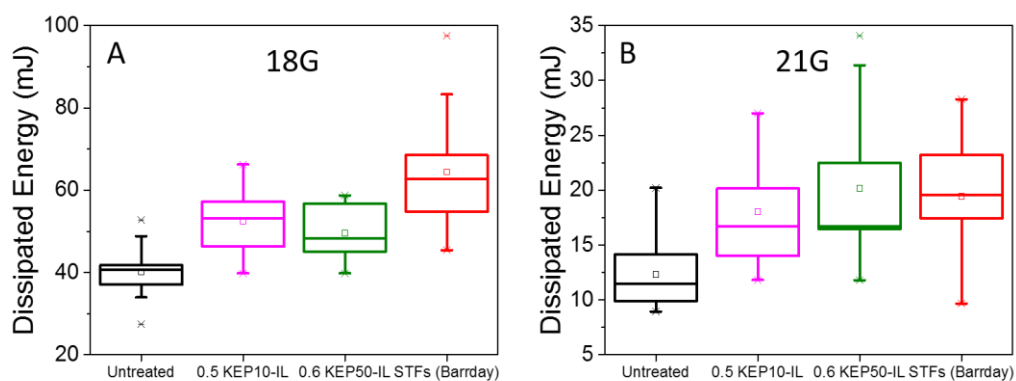


Figure 7.13: Box charts of dissipated energy during 18G (A) and 21G (B) needle penetration tests for Kevlar® 1148 before and after treated by various ionic liquid based and PEG based STFs.

Table 7.7: Summary of increased areal density (%), penetration peak forces, and dissipated energies during 18G needle penetration tests for Kevlar[®] 1148 before and after treatment by various ionic liquid based and PEG based STFs.

Treatment	Untreated	0.5 KEP10 IL	0.6 KEP50 IL	STFs (Barrday)
Increased Areal Density (%)	---	14.40 ± 0.81	23.97 ± 4.48	14.62 ± 2.24
Peak Force (N)	25.40 ± 3.55	35.70 ± 5.05	31.99 ± 5.50	38.84 ± 7.02
Dissipated Energy (mJ)	40.16 ± 6.52	52.54 ± 7.47	49.64 ± 6.67	64.41 ± 14.23

Table 7.8: Summary of increased areal density (%), penetration peak forces, and dissipated energies during 21G needle penetration tests for Kevlar[®] 1148 before and after treatment by various ionic liquid based and PEG based STFs.

Treatment	Untreated	0.5 KEP10 IL	0.6 KEP50 IL	STFs (Barrday)
Increased Areal Density (%)	---	14.40 ± 0.81	23.97 ± 4.48	14.62 ± 2.24
Peak Force (N)	9.11 ± 0.95	12.05 ± 1.38	12.88 ± 1.62	17.11 ± 2.84
Dissipated Energy (mJ)	12.33 ± 3.27	18.02 ± 5.61	20.16 ± 7.68	19.44 ± 5.55

7.4 Conclusions

Kevlar[®] 1148 fabrics were treated by ionic liquid [C₄mim][BF₄] based STFs. Because of the stability of ionic liquid under vacuum condition, the ionic liquid based STF-Kevlar[®] nanocomposites could be used in extreme space condition to provide protection against MMOD and stab threats. In this chapter, both spike and needle penetration tests were performed to evaluate the stab resistance of ionic liquid based STF-Kevlar[®] nanocomposites.

As ionic liquids are outstanding lubricants and are able to dissolve numerous polymers, there is the potential that the friction between fabric yarns could be reduced

and that the fiber could be dissolved, both of which would result in lowered penetration resistance. Therefore, the Kevlar[®] fabrics were treated with pure solvents and penetration tests were performed. The results show that the addition of ionic liquid to Kevlar[®] fabric has no obvious change in resistance capability in terms of penetration peak force and dissipated energy. Furthermore, the treatment condition for Kevlar[®] 1148 with ionic liquid based STF has been evaluated. The dilution ratio of ethanol to STF was found to be optimal at 3:1 volume ratio when the areal density, penetration peak force, and energy dissipation capability are considered.

Under the spike puncture threats, ionic liquid based STF-Kevlar[®] nanocomposites provide even better resistance against the threats than the PEG based STF-Kevlar[®] nanocomposites using the same treating condition in our lab. Furthermore, the lab-scale manufactured ionic liquid based STF-Kevlar[®] nanocomposites have comparable but slightly lower stab (spike puncture and needle cutting) resistant capability than the commercial PEG based STF-Kevlar[®] nanocomposites due to the potential difference in fabric treatment process. These experiments demonstrate that IL-based STF-Armor[™] has comparable performance to the PEG-based STF-Armor[™] previously used. Comparisons to commercial STF-Armor[™] formulations suggest that further improvements may be possible.

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Chapter 8

CONCLUSIONS AND FUTURE DIRECTIONS

8.1 Summary

Shear thickening fluid (STF)-nanocomposites (STF-ArmorTM) are a promising candidate material for use in extra-vehicular activity (EVA) suits to protect astronauts against threats of hypervelocity MMOD impacts and physical hazards from tools, and sharp edges.¹ The extreme environmental condition of space requires the development of novel STF formulations to be stable under vacuum and low temperature environment.

In this dissertation, I have developed novel STF formulations to be used in space conditions, and further, they have been successfully intercalated into aramid fabrics Kevlar[®] to form STF nanocomposites. The ionic liquid [C₄mim][BF₄] is used as the carrier medium for the new developed formulation due to its low volatility and high thermal stability. The stabilization mechanism, nanostructure, and dynamics of spherical silica particles dispersed in ionic liquid [C₄mim][BF₄] are investigated. With this knowledge, the primary goal of designing an ionic liquid based STF formulation is achieved. In support of this development work, the effect of water on the viscosity, density, and nanoscale structure of this ionic liquid are measured and analyzed within the framework of free volume theory. This insight provides guidance to formulate the rheological properties of ionic liquid colloidal dispersions. The major conclusions of this dissertation are summarized as follows and the directions for future research are suggested.

8.1.1 Ionic Liquids-Water Interaction and Phase Transition

Ionic liquids can easily absorb water from humid atmosphere and their thermodynamics properties and microstructure are altered significantly due to the presence of water. In order to develop ionic liquid colloidal dispersion formulations, it is thus crucial to understand the effect of water. The interaction between ionic liquid $[\text{C}_4\text{mim}][\text{BF}_4]$ and water molecules, the induced microstructure and phase behavior are examined in Chapter 3. The phase behavior of ionic liquid $[\text{C}_4\text{mim}][\text{BF}_4]$ -water mixtures covering the full composition range from high salt to low salt is investigated. With the addition of water into ionic liquid $[\text{C}_4\text{mim}][\text{BF}_4]$, there are four characteristic morphologies in the phase diagram: soluble water in ionic liquid with hydrogen bonding, water cluster formation, ionic liquid micellar aggregation, and dilute electrolyte solution.

At high salt levels, water molecularly dissolves into the network of ionic liquid $[\text{C}_4\text{mim}][\text{BF}_4]$ through hydrogen bonds, and a water-ionic liquid hydrogen bond network is formed without microphase separation. This hydrogen bonding is examined by studying the effects of added water molecules on the physical properties (density and viscosity) of ionic liquid $[\text{C}_4\text{mim}][\text{BF}_4]$ and the non-ideality of ionic liquid aqueous solutions. Densities and viscosities of the homogenous binary mixtures of $[\text{C}_4\text{mim}][\text{BF}_4]$ and water are measured for a temperature range of 283.15 to 373.15 K in the salt-rich regime. Excess molar volumes and non-idealities of the viscosities are calculated and discovered to be highly correlated. A new, semi-empirical correlation between the excess mixture viscosity and the excess molar volume in the salt-rich regime is identified, which is motivated by free volume theory. Additionally, a survey of the literature identifies ionic liquids with similar ionic structures for which this correlation is valid, which provides evidence for the role of specific molecular

interactions that govern the observed non-idealities in salt-rich mixtures of water in ionic liquids.

As the water concentration increases (over the salt-rich regime) to above ~ 70 mol%, a microphase transition to water nanoclusters resembling an inverse microemulsion is identified and characterized using small angle neutron scattering (SANS). In the salt-rich regime, water molecules are isolated and accommodated in the ionic liquid cation-anion polar network by interacting with anions and cations through hydrogen bonds. Such mixtures are a homogenous solution, with no significant changes in microstructure upon water addition as detected by SANS measurement. Water starts to form clusters when the molecular ratio of water to ionic liquid exceeds $\sim 2:1$, as expected from molecular structure standpoint. Distinct nanometer-sized water clusters form and grow with increase of water content, and water continues to partition between the dissolved state and microphase separated state.

On the other hand, ionic liquid $[\text{C}_4\text{mim}][\text{BF}_4]$ forms micellar aggregates at low salt regime due to the amphiphilic structural properties of cation $[\text{C}_4\text{mim}]^+$, which is revealed by small-angle x-ray scattering (SAXS). The CMC of $[\text{C}_4\text{mim}][\text{BF}_4]$ in H_2O is determined to be 0.8 mol/L, which is consistent with previous literature results.²⁻³ Spherical micelles of ionic liquid are formed at concentrations above CMC; however, micelles grow to ellipsoid rod shape as ionic liquid concentration increases. A “rod” like micellar structure is observed at higher concentration.

These observations establish a full phase diagram of ionic liquid aqueous solutions (microphase separation, phase inversion, and micelle formation) with addition of water, revealing similarities to traditional oil-water-surfactant systems. These results provide direct confirmation for recent simulations, as well insight into

the source of non-idealities in some thermophysical and transport properties (e.g. density and viscosity) of salt-rich aqueous mixtures reported in literature. These complex phase transitions of aqueous solutions of ionic liquid [C₄mim][BF₄] and the non-ideal viscosity behavior provide a guidance for the following rheological measurements of ionic liquid colloidal suspensions in this dissertation. In order to reduce the effect of absorbed humidity water on the viscosity and microstructure measurements, all the suspensions are dehydrated before measurements and fresh suspensions are used for each test.

8.1.2 Stabilization Mechanism and Interfacial Structure of Silica Particles in Ionic Liquids

Dispersing spherical silica particles into ionic liquids is challenging as the electrostatic repulsive forces are screened due to the high ionic strength nature of ionic liquids; thus, silica particles intend to aggregate as a result from the dominated van der Waals attraction. However, stable particle dispersion is crucial for shear thickening properties. Herein, a method to spontaneously disperse silica particles in ionic liquid [C₄mim][BF₄] is developed by inducing solvent structuring around the surface of the particle. The model system studied consists of spherical silica particles of ~ 100 nm size with 10% polydispersity, which are coated by fluorocarbon 1H,1H,9H hexadecafluoro-1-nonanol through dehydration reaction following the procedure of van Helden *et al.*⁴ The surface coating is confirmed by ¹H NMR and the grafting density is determined to be 1.4 chain/nm² with 60 % surface coverage using TGA (Chapter 4).

The stabilization mechanism and the corresponding interfacial structure of the fluorocarbon coated silica particles in ionic liquid [C₄mim][BF₄] are revealed in

Chapter 5. Solvent structured layers on the surface of particles, which are initiated by the hydrogen bonding between coated fluorocarbon and anion $[\text{BF}_4]^-$, are proven to provide sufficient steric stabilization against the dispersion attractions and result in stable colloidal silica particles dispersed in ionic liquid. The thickness of the solvation layers on the surface of particles is determined to be approximately 5 nm through extensive and independent characterization techniques, including dynamic light scattering (DLS), SANS, transmission electron microscopy (TEM), and rheology. The thickness of the solvation layers, which corresponds to seven ion-pair layers, is quantitatively consistent with previous studies on ionic liquid structuring near confined flat mica surfaces.⁵⁻⁸ Additionally, it is assumed for simplicity that the solvation layers form a well-defined, uniform shell surrounding the nanoparticles. However, the solvation layers near flat substrates are examined to become less organized and smoothly transition to the bulk liquid, as shown by experimental measurements^{5-6, 9-11} and simulations¹².

This designer surface coating on the particles alters specific molecular interactions between the particle surface and the ionic liquid. The induced solvent structuring is demonstrated as an effective method to create spontaneous dispersion and stabilization of nanoparticles that are otherwise not dispersible in ionic liquids. With the additional repulsion force from the solvation layer, silica particles are able to form stable suspensions in ionic liquid up to 61 wt% (corresponding to 45 vol%) solid content, which is a significant improvement on the current published maximum of 20 wt% particle content. These comprehensive results for fluorinated silica particle dispersions and the solvation layer mechanism not only provide a database for testing the proposed stabilization mechanism, but also act as a guidance for the development

of stable ionic liquid based shear thickening fluids formulation through the design of surface coatings.

8.1.3 Ionic Liquids Based Shear Thickening Fluids and Thermal Response

Silica particles coated by fluorocarbon have been demonstrated to be stable in ionic liquid $[\text{C}_4\text{mim}][\text{BF}_4]$ with the presence of 5 nm solvation layering structure around the particle surface. However, this stable fluorinated silica particle dispersion only exhibits mild shear thickening properties, which is not sufficient for the desired protection against multiple threats. Thus, a new ionic liquid based colloidal formulation system which demonstrates significant shear thickening behavior is crucial.

In chapter 6, stable ionic liquid based shear thickening colloidal dispersions have been formulated through the design of the particle surface chemistry. An alcohol hydrocarbon coated silica particle system is formulated. At room temperature, this concentrated silica nanoparticle dispersion in $[\text{C}_4\text{mim}][\text{BF}_4]$ displays stronger shear thickening than the previous studied fluorocarbon coated silica particle system. This is shown to be a consequence of a thinner solvation layers (~ 3 nm) initiated by relatively weaker hydrogen bonds between the hydrocarbon surface coating and anion group. In comparison to the strong hydrogen bonds between fluorinated surface and the anion, the hydrogen bonds between the alcohol hydrocarbon surface and the anion are much weaker. This 3 nm solvation layers provides sufficient stabilization force between particles, while still allowing the particles to approach together and shear-thicken at high shear rate/stress. This finding provides valuable insights for formulating stable, shear thickening dispersions in ionic liquids. Additionally, the alcohol hydrocarbon coated silica particles in ionic liquid suspension displays similar

shear thickening response as that of silica particles in polyethylene glycol (PEG), and thus, this formulation is promising to provide similar protection as PEG based STF's when intercalated with textiles.

Furthermore, the colloidal stability induced by the formation of solvation layers is found to be influenced by temperature. An increase of particle attraction and loss of stability of colloidal dispersions above 30 °C is discovered through rheological and SANS measurements. The mechanism driving increased particle attraction with increasing temperature is shown as a consequence of a reduction in the solvation layer thickness due to weakening hydrogen bonds between anion $[\text{BF}_4]^-$ and the surface. SANS and DLS measurements confirm the reduction of solvation layering thickness at elevated temperatures, revealing a transition from stable dispersion to unstable, attractive gel. This transition is compared with the established AHS particle state diagram. Because of the fundamentally different stabilization mechanisms, the gel transition at high temperature herein is in the opposite direction of traditional reported gel transition for coated particles dispersions at low temperatures.¹³⁻¹⁴ This investigation of a novel gel transition at high temperatures (*i.e.*, an inverse melting transition), the surface solvation structure, and the corresponding interparticle potential provide a model study for designing materials through surface modification and temperature control.

8.1.4 Protective Properties of Ionic Liquids Based STF-ArmorTM

With the successful development of ionic liquid based shear thickening fluid formulation as described in Chapter 6, the ionic liquid based STF-Kevlar[®] nanocomposites are fabricated and their stab resistance performance is evaluated using spike and needles (18 G, 21G) penetration tests.

Prior to the penetration tests on the ionic liquid based STF-Kevlar[®] nanocomposites, the effect of changing the solvents from traditional STF carrier medium, PEG, to ionic liquid [C₄mim][BF₄] is evaluated. Ionic liquids are outstanding lubricants and can dissolve numerous polymers, thus it is possible to have dissolved fiber and a lower penetration resistance with reduced friction between fabric yarns when treated with ionic liquids. However, our study indicates no obvious change in resistance capability for the different solvents treatments.

Thus, with the proof that the addition of ionic liquid to Kevlar[®] fabric does not change the protection performance of fabric itself, the treatment condition for Kevlar[®] 1148 with ionic liquid based STFs has been evaluated. The dilution ratio of ethanol to STFs was found to be optimized at 3:1 volume ratio when the areal density, penetration peak force, and energy dissipation capability are considered.

The stab resistance of the lab-scale manufactured ionic liquid based STF-Kevlar[®] against threats from a spike and 21 & 18 gauge needles are compared with (lab-scale manufactured and commercial) PEG-based STF-Kevlar[®]. It is found that ionic liquid based STF-Kevlar[®] nanocomposites provide even better resistance than the lab-scale manufactured PEG-based STF-Kevlar[®] nanocomposites against the spike puncture hazards. Furthermore, ionic liquid based STF-Kevlar[®] nanocomposites have comparable, but slightly lower, stab (spike puncture and needle cutting) resistant capability than the commercial PEG based STF-Kevlar[®] nanocomposites due to the potential difference in fabric treatment process. These findings suggest that IL-based STF-Armor[™] has comparable performance to the PEG-based STF-Armor[™] previously used. Further improvements may be possible with implanting same fabric treatment process as commercial STF-Armor[™]. Overall, the research completed in

this dissertation provides promising new ionic liquid based STF-nanocomposites for astronaut protection.

8.2 Recommendations for Future Work

Ionic liquids are chosen as the carrier medium for the novel STF formulations due to their low volatility and thermal stability which ensure the ability to flow under vacuum and extreme temperatures space environmental condition. In this dissertation, shear thickening behavior have been observed when performing rheological measurements on the ionic liquid based STF formulations under atmosphere and room temperature condition. The rheological response of the ionic liquid based STF formulations at high temperatures has also been investigated. However, it is of importance to measure their accurate and precise rheological response at simulated low-pressure/low temperature environmental conditions because they are aimed to be used for application in space. Preliminary results for the rheological responses of the ionic liquid based STF are achieved at simulated extreme low temperature using environmental test chamber (ETC) oven and extra low-pressure environment using the designed vacuum cell as described in Chapter 2.

The liquid state of ionic liquids at extreme low temperature has been proven as shown in Figure 8.1. The viscosity of ionic liquid $[C_4mim][BF_4]$ is measured inside the ETC oven with temperature decreasing from 10 °C to -80 °C at a rate of 5 °C/min. The temperature inside the ETC oven is controlled by liquid nitrogen. It is obvious that when the temperature reaches -65 °C, the torque no longer increases and the shear rate drops significantly, which indicates the freezing of ionic liquid $[C_4mim][BF_4]$. Thus, $[C_4mim][BF_4]$ is shown to be in the liquid state above -65 °C; this broad liquid state range is suitable for space applications. Furthermore, shear thickening behavior

is observed for concentrated silica particles-[C₄mim][BF₄] dispersions at extreme low temperature. Figure 8.2 displays an example of the rheological properties of $\phi = 0.4$ KE-P10 silica particles in [C₄mim][BF₄] at temperature down to -40 °C. The dispersion exhibits shear thickening behavior at the 25 °C to -40 °C temperature range studied. The order-of magnitude higher viscosity with decreasing temperature is expected as the ionic liquid solvent is approaching its freezing point. Additionally, the relative viscosity follows a general master curve, indicating no significant change in the microstructure at the temperature range studied. Note, there are slight increases in shear thickening strength and yielding at low shear stress at -40 °C. These may come from the structure rearrangement of ionic liquid when [C₄mim][BF₄] enters into glass state before freezing completely. Future researchers should study the structure of ionic liquid at the close to-freezing state, which aids to understand the particle interaction and hydrocluster formation under these extremely low temperatures.

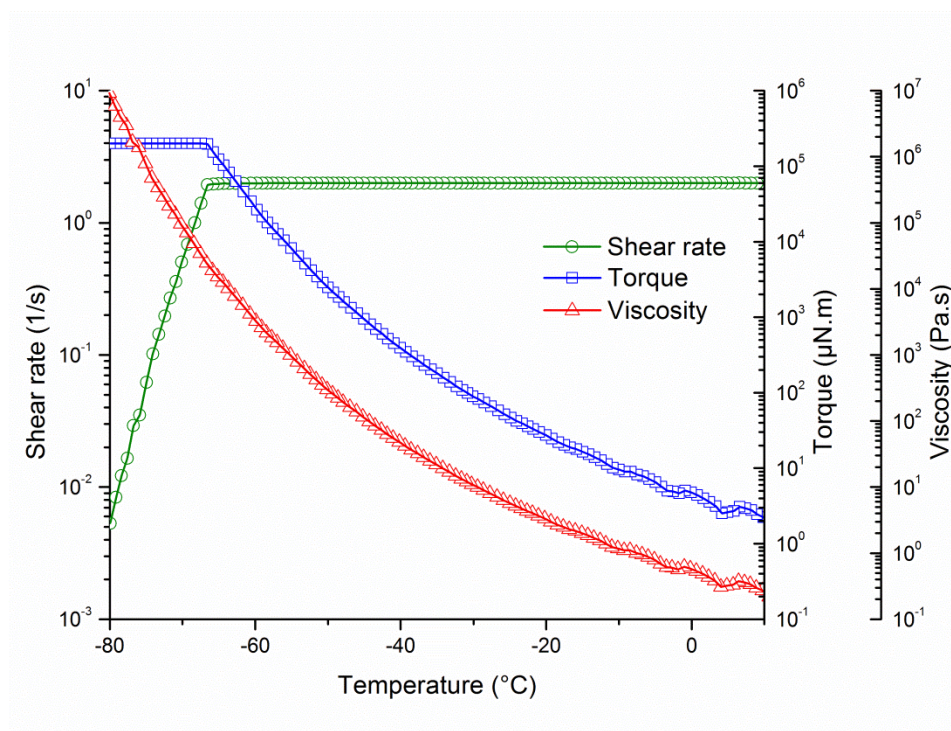


Figure 8.1: The rheological response of ionic liquid $[C_4mim][BF_4]$ using temperature sweep measurements with shear rate $2 s^{-1}$ under atmospheric condition. Temperature starts from $10^{\circ}C$ and cools down to $-80^{\circ}C$ at a cooling rate of $5^{\circ}C/min$.

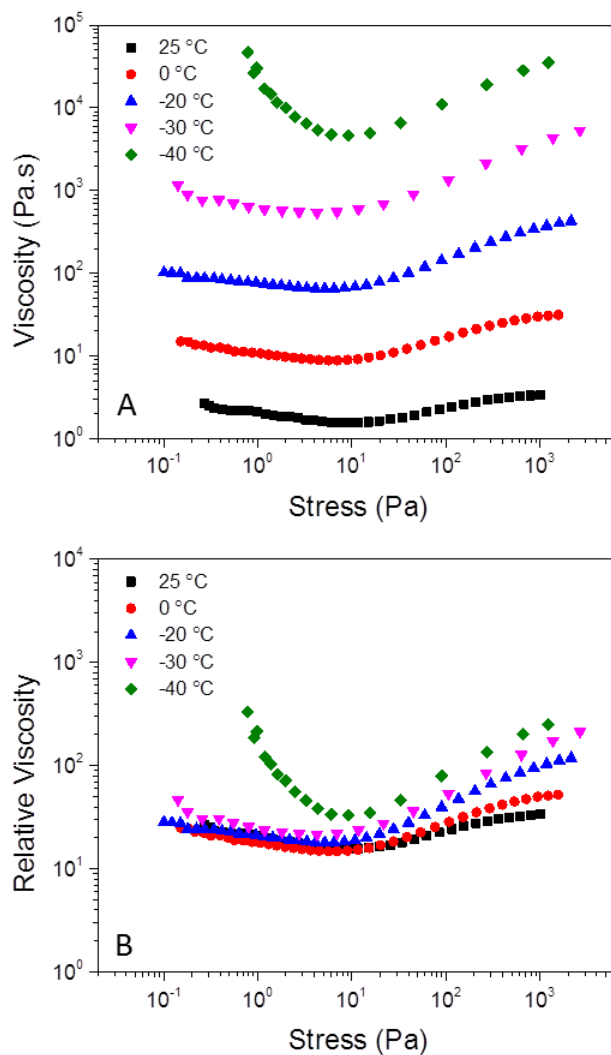


Figure 8.2: Steady state viscosity (A) and relative viscosity (B) as a function of shear stress at various temperature from 25 °C to -40 °C for $\phi = 0.4$ KE-P10 silica particles in [C₄mim][BF₄] under atmospheric condition.

A vacuum environment is achieved by using the vacuum cell described in Figure 2.3. Pressure as low as 10⁻⁶ torr is reached inside the vacuum cell within one hour using the turbo-pump station and the pressure curve is shown in Figure 8.3A.

The steady state flow curve of $\phi = 0.4$ KE-P10 silica particles in $[\text{C}_4\text{mim}][\text{BF}_4]$ at low pressure 10^{-6} torr is measured at 25 °C and compared with that measured at atmosphere condition in Figure 8.3B. The dispersion at this low pressure condition displays similar shear thickening behavior as for atmospheric conditions with the same critical shear stress and shear thickening strength. However, the shear viscosity of the dispersion is systematically higher at the low pressure condition, which may be the results of evaporating residual water or air bubbles at the extreme low pressure condition. Further research will be needed to address this question and identify the source of increased viscosity. Some improvements can be made for the vacuum cell setup, such as addition of de-gas mesh screen and tubing to accelerate the de-gassing procedure and allow liquid flow back to test cell after being de-gassed; installation of control unit to control the pressure inside the cell to desired value. Further improvement can be achieved by introducing low-temperature heat transfer fluids (temperature can reach as low as -110 °C) to the vacuum cell jacket, thus the rheological response of STFs can be measured at simulated low temperature/vacuum space condition.

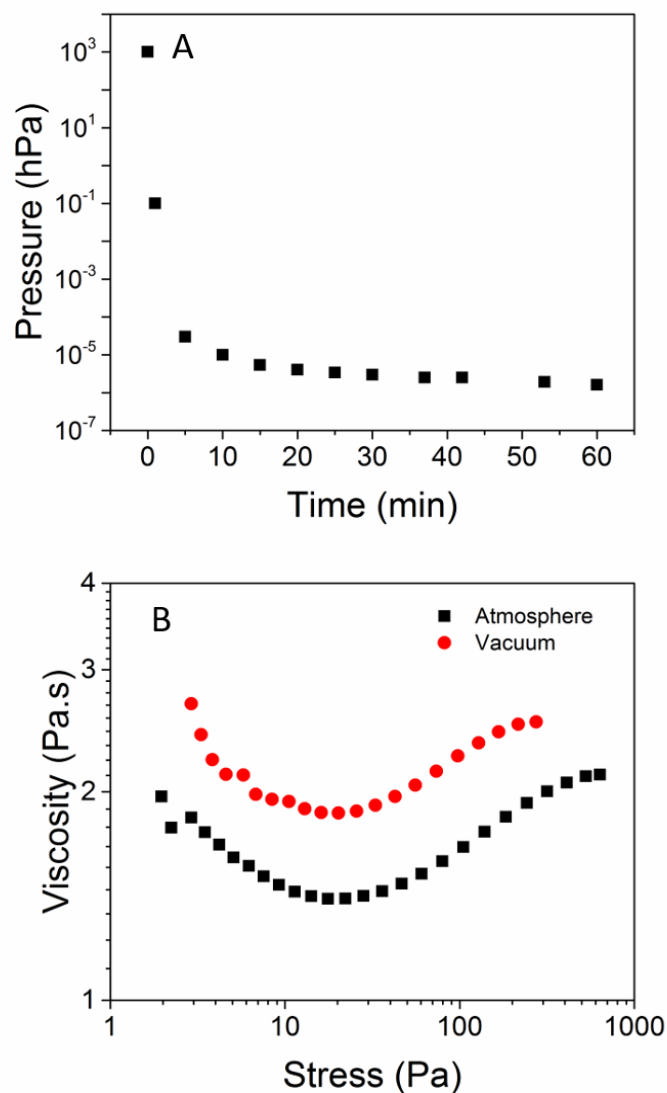


Figure 8.3: A) The pressure change inside the vacuum cell chamber as a function of time when the turbo-pump station starts to work at 25 °C. B) Comparison of the steady state viscosity of $\phi = 0.4$ KE-P10 silica particles in $[\text{C}_4\text{mim}][\text{BF}_4]$ at 25 °C under atmospheric and 10^{-6} hPa vacuum conditions.

The ionic liquid based STF formulations developed in this dissertation have shown distinguished shear thickening behavior not only at room temperature, but also under extreme low temperature and vacuum condition. However, the shear thickening property disappears at high temperatures due to the loss of particle stability. This is because the strength of the hydrogen bonds decreases with increasing temperature,¹⁵⁻¹⁶ and the solvation layers initiated by hydrogen bonds between surface coating and anion group of $[\text{C}_4\text{mim}][\text{BF}_4]$ are also interrupted. The thermal sensitivity of colloidal stability and the corresponding rheological response can be adjusted through replacing the hydrogen bonds with other physical/chemical bonds, such as ionic bonds or covalent bonds, which are less sensitive to temperature. For example, a hydrocarbon chain with a functional group of strong charge on one chain end (either positive or negative charge) and hydroxyl group on other chain end can be covalently coated onto the silica particle surface through the same dehydration reaction⁴ discussed in this dissertation. Thus, the surface of silica particles are fully covered by positive or negative charge, which will initiate the solvation layers through ionic bonding between positive surface charge and anion $[\text{BF}_4]^-$ or between negative surface charge and cation $[\text{C}_4\text{mim}]^+$. As the ionic bonds are nearly temperature independent, the solvation layers and the particle stability will be insensitive to temperature; thus, the shear thickening rheological response should also be temperature independent.

The developed novel ionic liquid based STF formulation displays similar rheological shear thickening behavior as that of PEG-based STF. Moreover, the fabricated ionic liquid based STF-Kevlar[®] nanocomposites are proved to provide even better resistance against the stab threats than the PEG based STF-Kevlar[®] nanocomposites through quasi-static puncture tests in this dissertation. As for the

space protection application against MMOD impact, their protective performance needs to be evaluated under simulated hypervelocity tests of high energy and short time scale. It has been reported that PEG based STF-ArmorTM provides enhanced protection against simulated hypervelocity MMOD impacts, with higher energy absorption capability than prototype lay-ups of the standard thermal micrometeoroid garment (TMG).¹ The damage of the PEG based STF-ArmorTM textile mainly comes from the burning and evaporating of textile layer. Compared with PEG solvent, most of ionic liquids are non-flammable and do not evaporate; thus, they have the potential to provide better protection against hypervelocity impact when using ionic liquid based STF-ArmorTM. Hypervelocity tests on ionic liquid based STF-ArmorTM will be crucial to verify this hypothesis in the future research.

A further step after the simulated MMOD hypervelocity test on STF-ArmorTM performed on Earth is having the STF-ArmorTM materials tested in the real space environment experiencing the MMOD impact threats. A proposal for NASA's Materials on International Space Station Experiment (MISSE) have been awarded to University of Delaware for the investigation of MMOD hypervelocity impact resistance of TMG prototype lay-ups with STF-ArmorTM absorber layers under the real low-earth orbit (LEO) environment. Flying over 200 miles above Earth, fixed to the exterior of the International Space Station (ISS) for a period of one year, the TMG lay-ups will endure extreme harsh environment of LEO: MMOD impact, vacuum, atomic oxygen, solar and charged-particle radiation, direct sunlight and extreme temperature. The experiment will provide a better and direct understanding of material durability and hypervelocity impact resistance of STF-ArmorTM in the real

LEO environment, which will be greatly beneficial for the designer STF-Armor™ material for space protective application.

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Appendix A

SUPPORTING INFORMATION FOR CHAPTER 3

Table A.1: Summary of experimental density ρ , viscosity η , density deviation $\Delta\rho$, excess molar volume V^{ex} and excess log viscosity $(\log\eta)^{\text{ex}}$ of [C₄mim][BF₄] aqueous solutions at various temperatures.

T (K)	Water content (wt%)						
	0.00	0.28	0.52	1.01	2.03	3.01	5.00
ρ (g/cm ³)							
283.15	1.21203	1.21100	1.21008	1.20846	1.20535	1.20215	1.19586
293.15	1.20479	1.20376	1.20281	1.20118	1.19807	1.19485	1.18852
298.15	1.20117	1.20014	1.19920	1.19757	1.19446	1.19123	1.18486
303.15	1.19758	1.19655	1.19561	1.19398	1.19086	1.18762	1.18122
313.15	1.19045	1.18943	1.18848	1.18685	1.18370	1.18042	1.17395
323.15	1.18341	1.18237	1.18141	1.17977	1.17660	1.17330	1.16673
333.15	1.17642	1.17538	1.17441	1.17275	1.16954	1.16620	1.15953
343.15	1.16949	1.16843	1.16746	1.16578	1.16255	1.15916	1.15240
353.15	1.16261	1.16155	1.16056	1.15886	1.15558	1.15215	1.14532
363.15	1.15578	1.15370	1.15370	1.15198	1.14866	1.14518	1.13827
$\Delta\rho$ (g/cm ³)							
283.15	0	-0.00031	-0.00061	-0.00098	-0.00147	-0.00217	-0.00342
293.15	0	-0.00033	-0.00068	-0.00110	-0.00167	-0.00247	-0.00392
298.15	0	-0.00034	-0.00069	-0.00112	-0.00173	-0.00257	-0.00413
303.15	0	-0.00035	-0.00070	-0.00115	-0.00180	-0.00268	-0.00433
313.15	0	-0.00036	-0.00073	-0.00120	-0.00194	-0.00290	-0.00471
323.15	0	-0.00039	-0.00078	-0.00128	-0.00207	-0.00310	-0.00508
333.15	0	-0.00039	-0.00081	-0.00134	-0.00220	-0.00329	-0.00543
343.15	0	-0.00042	-0.00084	-0.00140	-0.00230	-0.00346	-0.00572
353.15	0	-0.00042	-0.00086	-0.00145	-0.00241	-0.00362	-0.00598
363.15	0	-0.00044	-0.00089	-0.00150	-0.00250	-0.00377	-0.00621
V^{ex} (cm ³ /mol)							
283.15	0	0.047	0.089	0.135	0.185	0.251	0.342

293.15	0	0.051	0.100	0.154	0.213	0.289	0.396
298.15	0	0.052	0.102	0.158	0.222	0.303	0.420
303.15	0	0.054	0.105	0.163	0.232	0.318	0.442
313.15	0	0.055	0.110	0.173	0.252	0.348	0.488
323.15	0	0.061	0.119	0.186	0.273	0.376	0.532
333.15	0	0.063	0.124	0.197	0.294	0.404	0.576
343.15	0	0.067	0.131	0.208	0.310	0.430	0.614
353.15	0	0.069	0.136	0.218	0.329	0.455	0.649
363.15	0	0.073	0.143	0.229	0.346	0.480	0.682

η (mPa.s)

293.15	133.48 ± 0.86	115.23 ± 0.43	102.19 ± 0.51	81.44 ± 0.31	56.26 ± 0.15	42.00 ± 0.31	26.68 ± 0.30
298.15	101.39 ± 0.74	88.77 ± 0.33	79.43 ± 0.28	64.34 ± 0.19	45.35 ± 0.16	34.43 ± 0.31	22.34 ± 0.33
303.15	78.84 ± 0.41	69.82 ± 0.18	63.06 ± 0.12	51.73 ± 0.14	37.18 ± 0.20	28.67 ± 0.32	18.95 ± 0.34
313.15	50.52 ± 0.20	45.58 ± 0.05	41.37 ± 0.72	35.01 ± 0.08	26.09 ± 0.24	20.59 ± 0.34	14.10 ± 0.37
323.15	34.52 ± 0.10	31.56 ± 0.13	29.13 ± 0.23	25.01 ± 0.20	19.17 ± 0.28	15.49 ± 0.36	10.89 ± 0.36
333.15	24.86 ± 0.13	22.98 ± 0.22	21.40 ± 0.27	18.67 ± 0.25	14.66 ± 0.30	12.06 ± 0.37	8.67 ± 0.33
343.15	18.69 ± 0.20	17.44 ± 0.26	16.34 ± 0.33	14.45 ± 0.29	11.59 ± 0.32	9.64 ± 0.35	7.11 ± 0.31
353.15	14.54 ± 0.25	13.67 ± 0.31	12.87 ± 0.35	11.50 ± 0.31	9.40 ± 0.33	7.91 ± 0.33	5.98 ± 0.30
363.15	11.64 ± 0.28	11.00 ± 0.32	10.40 ± 0.36	9.39 ± 0.31	7.79 ± 0.32	6.65 ± 0.30	5.16 ± 0.29
373.15	9.55 ± 0.30	9.06 ± 0.32	8.60 ± 0.34	7.83 ± 0.31	6.60 ± 0.31	5.71 ± 0.30	4.54 ± 0.29

$(\log \eta)^{ex}$ (log(mPa.s))

293.15	0	0.008 ± 0.002	0.015 ± 0.002	0.027 ± 0.002	0.064 ± 0.001	0.094 ± 0.003	0.147 ± 0.005
298.15	0	0.012 ± 0.002	0.021 ± 0.002	0.036 ± 0.001	0.076 ± 0.002	0.108 ± 0.004	0.162 ± 0.007
303.15	0	0.015 ± 0.001	0.026 ± 0.001	0.044 ± 0.001	0.086 ± 0.002	0.121 ± 0.005	0.175 ± 0.008
313.15	0	0.019 ± 0.001	0.030 ± 0.008	0.055 ± 0.001	0.103 ± 0.004	0.140 ± 0.007	0.198 ± 0.011
323.15	0	0.022 ± 0.002	0.037 ± 0.003	0.064 ± 0.003	0.117 ± 0.006	0.157 ± 0.010	0.216 ± 0.014
333.15	0	0.025 ± 0.004	0.042 ± 0.006	0.072 ± 0.006	0.128 ± 0.009	0.171 ± 0.013	0.230 ± 0.017
343.15	0	0.027 ± 0.076	0.045 ± 0.009	0.077 ± 0.009	0.137 ± 0.012	0.180 ± 0.016	0.243 ± 0.019
353.15	0	0.028 ± 0.010	0.047 ± 0.012	0.081 ± 0.012	0.144 ± 0.015	0.188 ± 0.018	0.256 ± 0.022
363.15	0	0.029 ± 0.013	0.048 ± 0.015	0.085 ± 0.015	0.150 ± 0.018	0.197 ± 0.020	0.271 ± 0.025
373.15	0	0.029 ± 0.015	0.049 ± 0.017	0.088 ± 0.017	0.156 ± 0.020	0.206 ± 0.023	0.286 ± 0.028

Table A.2: Fitting parameters of the Redlich-Kister equation for excess molar volume $\underline{V}^{ex}$ and density deviation $\Delta\rho$ of dependence on water molar fraction x_w for [C₄mim][BF₄] aqueous solutions at varying temperatures.

T (K)	$\underline{V}^{ex}$ (cm ³ /mol)				$\Delta\rho$ (g/cm ³)			
	A_0	A_1	A_2	A_3	A_0	A_1	A_2	A_3
283.15	1.52	-0.05	-3.19	-3.53	0.018	0.018	0.005	0.018
293.15	1.82	0.38	-2.69	-3.35	0.021	0.024	0.001	0.016
298.15	1.94	0.54	-2.66	-3.39	0.022	0.027	0.003	0.015
303.15	2.06	0.66	-2.62	-3.40	0.024	0.029	0.005	0.015
313.15	2.28	0.80	-2.70	-3.46	0.026	0.032	0.006	0.014
323.15	2.54	1.22	-2.37	-3.48	0.028	0.039	0.012	0.012
333.15	2.80	1.72	-1.65	-3.05	0.031	0.043	0.019	0.009
343.15	2.96	1.62	-2.33	-3.64	0.032	0.044	0.017	0.012
353.15	3.15	1.91	-1.84	-3.30	0.034	0.047	0.021	0.009
363.15	3.28	1.74	-2.51	-3.82	0.035	0.047	0.017	0.012

Table A.3: Fitting parameters of the exponential function Equation 3-4 of the viscosity dependence on water molar fraction for [C₄mim][BF₄] aqueous solutions at different temperatures.

T (K)	a
293.15	0.24
298.15	0.26
303.15	0.27
313.15	0.31
323.15	0.35
333.15	0.39
343.15	0.42
353.15	0.46
363.15	0.49
373.15	0.54

Density deviations from ideal mixing with respect to water content and temperature

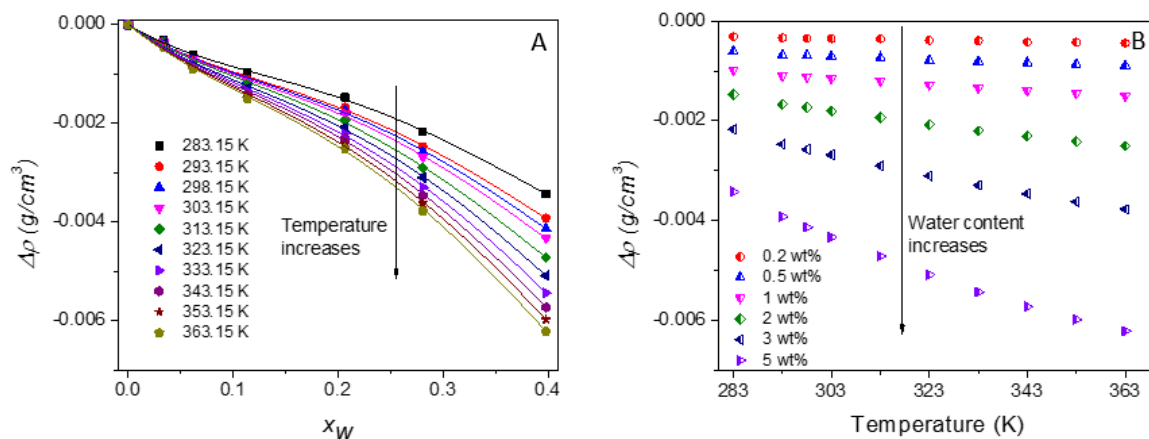


Figure A.1: Density deviations $\Delta\rho$ of [C₄mim][BF₄] aqueous solutions for varying water molar fraction x_w (A) and temperature (B). The symbols represent experimental value. The solid lines represent Redlich-Kister equation fitting.

The calculated density deviation $\Delta\rho$ of the binary ionic liquid aqueous mixtures from ideal mixing are plotted in Figure A.1. The values of $\Delta\rho$ of Figure A.1A at several temperatures are fitted to the Redlich-Kister polynomial equation:

$$\Delta\rho = x_w x_{IL} \sum_{i=0}^m A_i (x_w - x_{IL})^i \quad \text{A-1}$$

Where A_i are the fitting coefficients, m is the order of the Redlich-Kister polynomial equation, x_w and x_{IL} are the molar fraction of water and ionic liquid in the aqueous mixtures. The density deviations are negative for all the temperature and salt-rich compositions, and these deviations increase with water content and temperature.

Arrhenius equation fitting for viscosity dependence on temperature over various water contents for [C₄mim][BF₄] aqueous solutions

The mixture viscosities decrease with temperature and are fitted with Arrhenius equation for different water contents as shown in Figure A.2:

$$\eta = A \exp(E_a / RT) \quad \text{A-2}$$

where E_a is the activation energy. Compared with Vogel-Fulcher-Tammann (VFT) equation fitting, Arrhenius fitting shown in Figure A.2 is not able to quantitatively fit the entire range and deviations are noted especially at low water concentrations. The fitted activation energy values are listed in Table A.4.

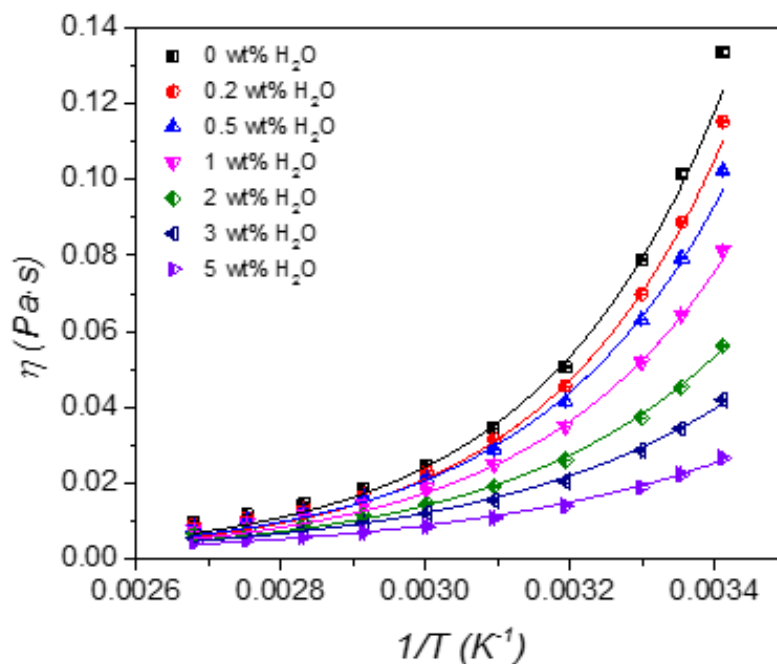


Figure A.2: The viscosities of [C₄mim][BF₄] aqueous solutions at different temperatures with Arrhenius equation fitting.

Table A.4: Fitting parameter (activation energy E_a) of the Arrhenius equation of [C₄mim][BF₄] aqueous solutions with various water contents.

Water content	A	E_a
wt %	$mPa \cdot s$	$kJ \cdot mol^{-1}$
0	1.7E-4	32.9
0.28	1.3E-4	33.4
0.52	2.7E-4	31.2
1.01	2.9E-4	30.5
2.03	6.6E-4	27.6
3.01	1.7E-4	24.6
5.00	3.5E-4	21.7

Derivation of semi-empirical linear correlation between excess molar volume and excess log viscosity from free volume theory

From free Volume theory,¹ the viscosity of fluid is related with molar free volume:

$$\log \eta = \log A + B \frac{V - V_f}{V_f} \quad A-3$$

As defined in the text, the excess mixture viscosity is defined as the deviation from the Arrhenius ideal solution mixing rule as:

$$\log \eta = x_{IL} \log(\eta_{IL}) + x_w \log(\eta_w) + (\log \eta)^{ex} \quad A-4$$

Substituting Equation A-3 into Equation A-4

$$\begin{aligned} \log \eta &= x_{IL} \log A_{IL} + x_w \log A_w + x_{IL} B_{IL} \frac{V_{IL} - V_{f,IL}}{V_{f,IL}} + x_w B_w \frac{V_w - V_{f,w}}{V_{f,w}} + \Delta(\log A) + \Delta(B \frac{V^{ex} - V_f}{V_f}) \\ (\log \eta)^{ex} &= \Delta(\log A) + \Delta(B \frac{V^{ex} - V_f}{V_f}) = (\Delta(\log A) - \Delta B) + \frac{B}{V_f} V^{ex} \end{aligned}$$

As it is global correlation, the correlation would valid for the simplest case – ideal mixing. For ideal mixing, $(\log \eta)^{ex} = 0$, $V_f^{ex} = 0$, thus I have $\Delta(\log A) - \Delta B = 0$.

Then, assuming A and B are independent of composition and temperature, the linear correlation between excess viscosity and excess molar volume is obtained:

$$(\log \eta)^{ex} = \frac{B}{V_f} V_f^{ex} \quad \text{A-5}$$

Examples of ionic liquids aqueous solution systems invalid for semi-empirical linear correlation of Equation 3-9

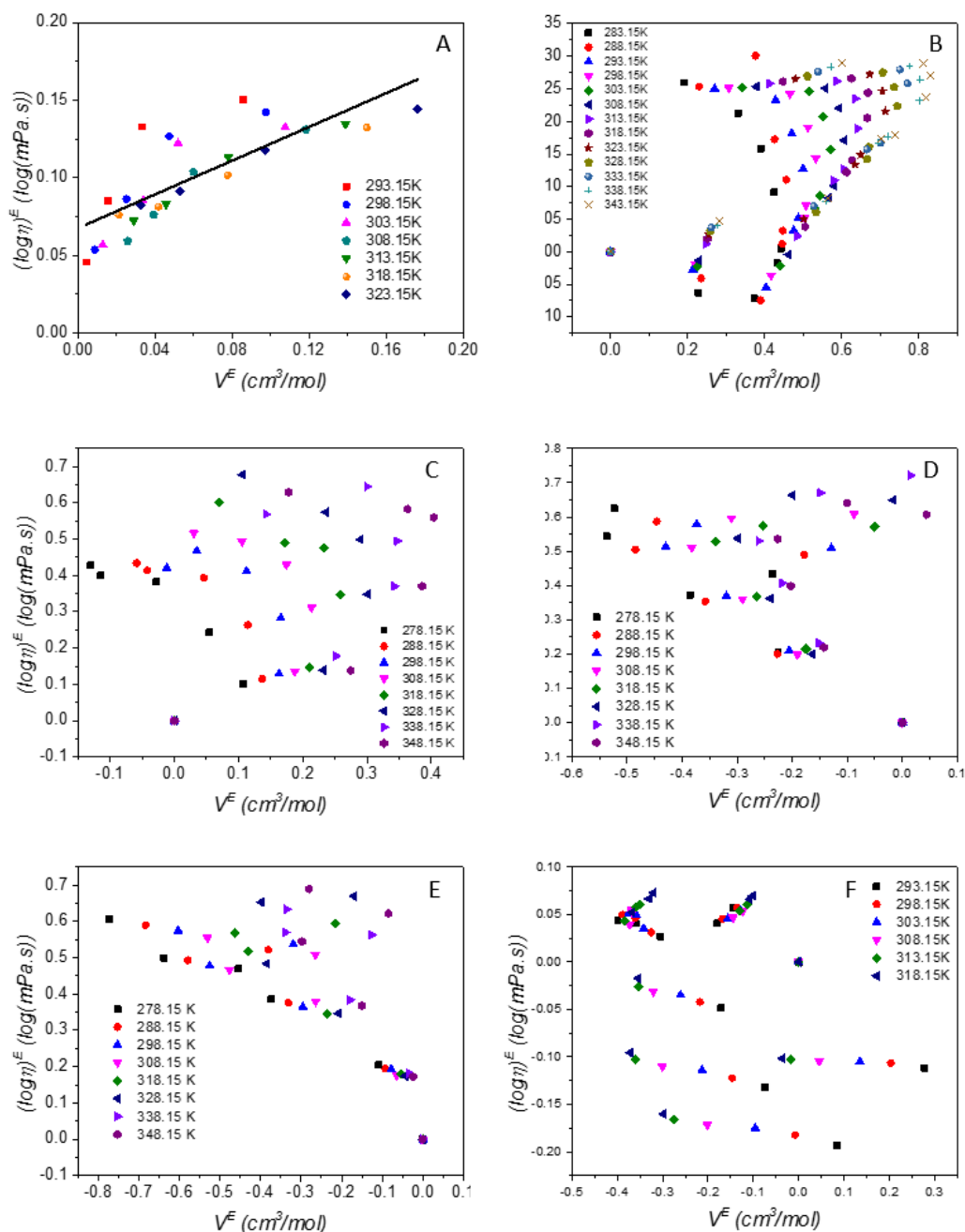


Figure A.3: Plots of excess log viscosity, $(\log \eta)^{ex}$, and excess molar volume, V^{ex} , of [C₂mim][BF₄] of salt-rich regime² (water molar fraction up to 40%) (A), [BuPy][BF₄]³ (B), [C₂mim][OTf]⁴ (C), [C₂mim][EtSO₄]⁴ (D), [C₂mim][TFA]⁴ (E), EAN⁵ (F) aqueous solutions over the entire range of water compositions.

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Appendix B

SHEAR RHEOLOGY OF FUMED AMORPHOUS SILICA PARTICLES IN IONIC LIQUID

In this appendix, the shear rheological behavior of fumed amorphous silica particles in ionic liquid $[C_4mim][BF_4]$ is investigated. The effects of sample preparation (i.e., mixing) protocol, silica particle size, and surface chemical on the particle stability and hence the rheological response are studied. BeadBeater mixing method is found to be the most efficient and reproducible mixing method. Fumed amorphous hydrophilic particles show similar critical shear stress dependence on the particle size as for the hard sphere silica particles. Hydrophilic fumed silica particles are stable in ionic liquid $[C_4mim][BF_4]$ due to the solvation layers and show shear thickening behavior, whereas hydrophobic fumed silica particles are unstable and exhibit shear thinning behavior.

B.1 Materials and methods

B.1.1 Materials

The silica nanoparticles (hydrophilic particles: Aerosil 90, 200, 380 and hydrophobic particles: Aerosil R104, R805) are obtained from the Degussa Corporation. The Aerosil particles consist of primary particles with a characteristic length of approximately 12 nm which form an agglomerated secondary structure. The interparticle physical bonds of the flocculated silica network can be disrupted by shear

force. All the particles are dried for 24 h in an oven at 120 °C before use. The distributions of the particle sizes have been characterized by dynamic light scattering (DLS) (Brookhaven particle size analyzer). Aerosil 90, 200, and 380 have the same hydrophilic surface chemistry - silanol groups on the surface.¹ Aerosil R104 and R805 are hydrophobic derivatives of silica particle (Aerosil 200), with the surface modified by octamethylcyclotetrasiloxane (D4) and octylsilane, respectively. As the direct derivatives of Aerosil 200, these silica particles (Aerosil 200, R104, and R805) are expected to have comparable particle sizes. Characteristics of particle, such as surface chemistry, particle size, and hydrophobicity are listed in Table B.1. Note that the hydrophobicity of the particle is determined by methanol wettability, such that higher methanol wettability indicates higher degree of hydrophobicity.

1-Butyl-3-methylimidazolium tetrafluoroborate ([C₄mim][BF₄], 99%, Mw=226.02 g/mol) is purchased from Iolitec Ionic Liquid Technologies. This ionic liquid is dehydrated under vacuum at 70 °C for 24 h prior to use. The water content of [C₄mim][BF₄] determined by the Karl Fisher titration is 373 ppm.

Table B.1: Characteristics of fumed amorphous particles.

Particles	Aerosil 90	Aerosil 200	Aerosil 380	Aerosil R104	Aerosil R805
A _S [*] (m ² /g)	90 ± 15	200 ± 25	380 ± 30	150 ± 25	150 ± 25
D _h ^{**} (nm)	271.7 ± 2.0	230.0 ± 0.9	201.9 ± 1.0	---	---
Surface chemical	-OH	-OH	-OH	octamethylcyclotetrasiloxane	octylsilane
Methanol wettability	---	---	---	~33% ¹	~47% ¹

* A_S is the specific surface area, obtained from ref¹

** D_h is the hydrodynamic diameter determined by DLS

B.1.2 Preparation of colloidal dispersions in [C₄mim][BF₄]

Colloidal suspensions are formulated by dispersing different silica particles in [C₄mim][BF₄]. Three standard mixing devices are employed to homogenize the silica colloidal dispersions and to investigate the impact of mixing methods on the rheological behavior: a Vortex mixer (Fisher Scientific, 150watts), a Silverson lab mixer (L4RT, 5/8" Micro Tubular frames, Silverson), and a BeadBeater (MiniBeadBeater-1, Biospec). The mixing procedures for the Vortex mixer, the Silverson lab mixer, and BeadBeater are: 3000 rpm for 5 min, 5000 rpm for 5 min, and 5000 rpm for 5 min, respectively. Homogenous dispersions are obtained by mechanical mixing followed by 10 min of degassing to remove any air bubbles in the samples. The samples are dehydrated again at 70 °C for 24 h under vacuum prior to rheological measurements.

B.1.3 Rheological measurements

For each colloidal silica dispersion, rheological measurements are performed on a stress-controlled rheometer (AR-G2, TA Instruments) with a Peltier temperature controller at 25 °C and a standard cone-plate geometry (1° cone angle, 40 mm diameter).

Previous investigations on the rheology of concentrated dispersions have shown that shear history can have a profound impact on the repeatability of results.²⁻³ To erase shear history on the samples and to establish their equilibrium structures, a steady pre-shear is applied at a shear stress of 10 Pa for 1 min followed by a 1 min equilibration period before each dynamic rheological measurement. The degree of dispersion homogeneity is assessed by the yield stress of suspensions, such that a lower yield stress indicates a better homogenous mixing. To determine the yield stress, a strain sweep oscillation test is performed at a constant frequency of 10 rad/s

with a strain range of 0.01% - 1000% at 25 °C. The shear thickening curve is obtained by using the following protocol: (1) a 1 min steady shear at shear stress 10 Pa followed by a 1 min equilibration; (2) a 10 min stress ramp back and forth from 0.001 Pa to 1500 Pa to remove shear history effects; (3) a 1 min steady shear at a shear stress of 10 Pa followed by a 1 min equilibration; (4) a steady state shear stress ramp back and forth sweep from 0.001 to 1500 Pa. The critical shear stress for shear thickening is defined as the shear stress value where increase in viscosity is first evident in the stress sweep curve. Finally, the slope of the viscosity versus shear stress in the shear thickening regime is used as a metric to determine the strength of the shear thickening transition.

B.2 Results and discussion

B.2.1 Effect of mixing methods

Ueno *et al.* reported that suspensions comprised of concentrated silica (Aerosil 200) in ionic liquid [C₄mim][BF₄] showed shear thickening behavior.² Similar suspensions comprised of Aerosil 200 silica particles in [C₄mim][BF₄] are investigated and their shear rheological behaviors are compared with reported results in Figure B.1. For 5 wt% of Aerosil 200 in [C₄mim][BF₄], the suspension exhibits a weak shear thickening behavior, while a much stronger shear thickening transition is observed for 10 wt% of Aerosil 200 in [C₄mim][BF₄]. This increase in shear thickening behavior with particle concentration is expected and is consistent with previous studies.⁴ When subjected to low and moderate shear rates, suspensions have a relatively low viscosity and behave as a liquid. However, at higher shear rates, rheological response of

suspension material changes to a solid-like behavior and the viscosity increases dramatically.⁵

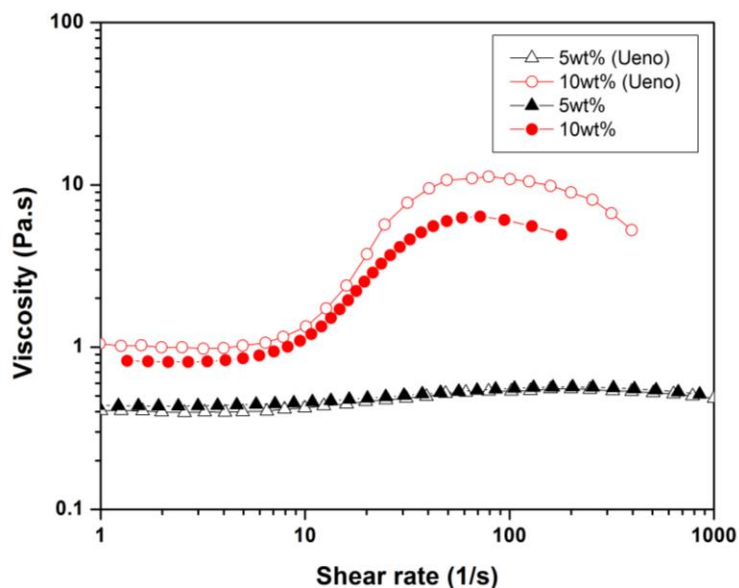


Figure B.1: Viscosity shear flow curves of silica particle Aerosil 200 in $[C_4mim][BF_4]$ with various particle contents and comparison with literature results by Ueno *et al.*²

As shown in Figure B.1, shear flow curves of Aerosil 200 suspensions are qualitatively comparable to the data reported by Ueno *et al.*; however, the suspension with 10 wt% silica content shows small quantitative differences with regards to the location and magnitude of the shear thickening peak. These deviations could be attributed to the different mixing protocols. Vortex mixers used for suspension preparations are quite different and less reproducible than that used by Ueno *et al.* (conditioning mixer AR-250). Therefore, investigations on the mixing methods are essential to obtain more reproducible and homogeneous suspensions. 10 wt%

suspensions Aerosil 200 in $[\text{C}_4\text{mim}][\text{BF}_4]$ are prepared and mixed by Vortex mixer, the Silverson mixer, and BeadBeater, respectively, and their steady shear flow curves are compared in Figure B.2. It is clear that suspension mixed by Beadbeater shows systematically lower value viscosity, indicating the most efficient and powerful mixing method. The flow curve of suspension mixed by Silverson mixer lays in between the ones mixed by Vorted mixer and BeadBeater. The characteristic parameters, such as critical stress, shear thickening strength from steady state shear flow curve, and yield stress from small amplitude oscillation shear curve for each samples are listed in Table B.2. As shown in Table B.2, suspension mixed by BeadBeater have the smallest yield stress than other mixing methods, which indicates a better homogeneity of suspension, and agrees with steady state flow curves discussed before. Thus, BeadBeater mixing method is used to prepare all the following Aerosil silica particle suspensions.

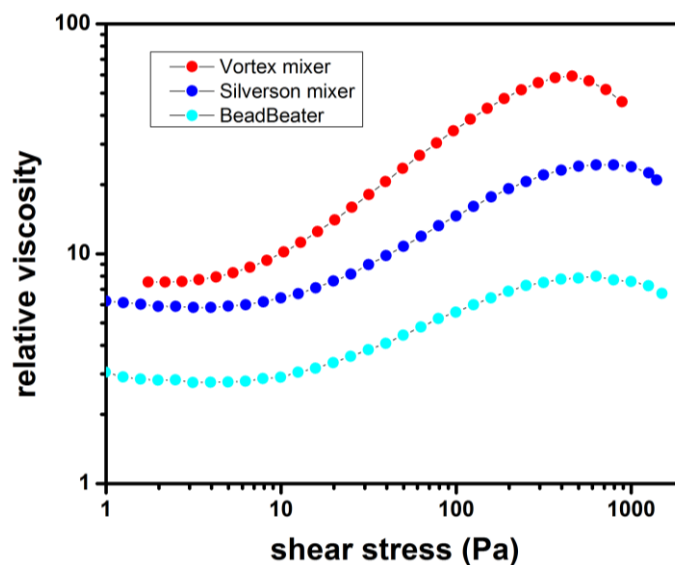


Figure B.2: Steady state shear flow curves of 10 wt% Aerosil 200 in $[C_4mim][BF_4]$ suspensions mixed by various methods.

Table B.2: Comparison of characteristic parameters for 10 wt% Aerosil 200 - $[C_4mim][BF_4]$ suspensions mixed with various methods.

	Vortex mixer	Silverson mixer	BeadBeater
Critical stress (Pa)	2.7 ± 0.7	4.0 ± 0.8	3.9 ± 0.8
Shear thickening strength	0.52 ± 0.01	0.37 ± 0.01	0.30 ± 0.01
Yield stress (Pa)	2.0 ± 0.4	1.9 ± 0.4	1.6 ± 0.2

B.2.2 Effect of particle size on shear thickening behavior

The impact of particle size on the rheological response of suspensions is studied using a series of hydrophilic silica particles (Aerosil 90, 200, and 380) of the same surface chemical (silanol group on the surface), but varying the surface area (particle size). All the suspensions are prepared and mixed using the same mixing method (BeadBeater) for consistency. The steady state shear flow curves of 10 wt% silica particle suspensions prepared using Aerosil 90, 200, and 380 are shown in

Figure B.3. Their characteristic parameters for each flow curve are given in Table B.3.

Suspension of larger particles size (Aerosil 90) exhibits a smaller critical stress and increased shear thickening strength, indicating an easier and more extreme shear thickening response. This is consistent with previous results of shear thickening fluids with solid sphere particles, larger particles tending to form hydroclusters at lower shear stress.⁶ However, Aerosil particle system shows a close but slightly lower critical stress when compared with solid hard sphere particle system of the equal apparent particle size under the same particle contents.³ This deviation is speculated to result from the intrinsic structure of the Aerosil particle system. The structure of the flocculated silica network can be disrupted by shear flow, resulting in new and unstable surfaces tending to form aggregations and gelation, which leads to a lower critical stress than the hard sphere system.

Table B.3: Comparison of characteristic parameters of 10 wt% hydrophilic silica particle (Aerosil 90, 200, and 380) -[C₄mim][BF₄] suspensions

	Aerosil 90	Aerosil 200	Aerosil 380
Critical stress (Pa)	2.0 ± 0.3	3.9 ± 0.8	7.9 ± 1.7
Hard sphere critical stress (Pa)	~3	~5	~12
Shear thickening strength	0.31 ± 0.01	0.30 ± 0.01	0.23 ± 0.01

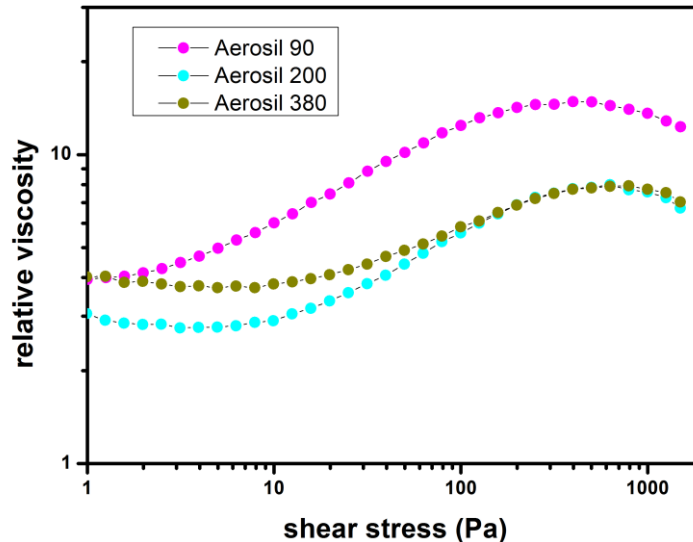


Figure B.3: Steady state shear flow curves of 10 wt% Aerosil hydrophilic silica particle suspensions of various particle sizes.

B.2.3 Effect of particle surface chemical on rheological behavior

Aerosil R104 and R805 are hydrophobic derivatives of Aerosil 200, with surface modified by octamethylcyclotetrasiloxane (D4) and octylsilane, respectively. Thus, fumed silica particles Aerosil 200, R104, and R805 have comparable particle sizes. The effect of particle surface chemical on suspension rheological properties can be investigated by using these particles with the same particle size. All the suspensions are mixed and prepared using the same mixer (BeadBeater) and protocol. Their rheological response of these silica particle suspensions of 10 wt% particle contents are shown in Figure B.4 and the yield stresses measured from small amplitude oscillation shear rheology are listed in Table B.4.

It is found that suspensions that are composed of more hydrophobic silica particles tend to form gelation under rest. A high yield stress value is found to be

associated with more hydrophobic silica particle suspension, indicating particles aggregating in ionic liquid, rather than dispersing. These observations demonstrate a fundamentally different inter-particle interactions of hydrophilic and hydrophobic silica particle in ionic liquid $[C_4mim][BF_4]$. For the hydrophilic particles, the surface silanol groups form hydrogen bonds with the anionic group of $[BF_4]^-$, resulting in an adsorbed anion layer on the silica particle surface. This induces a solvation layering effect which has been observed in previous studies.^{2,7} The formation of a solvation multilayer on the silica particle surface gives rise to a repulsive solvation force and stabilizes the silica particles as shown in Figure B.5; whereas for the hydrophobic silica particles, no solvation layers are formed, such that particles are not stable and tend to aggregate in the ionic liquids.

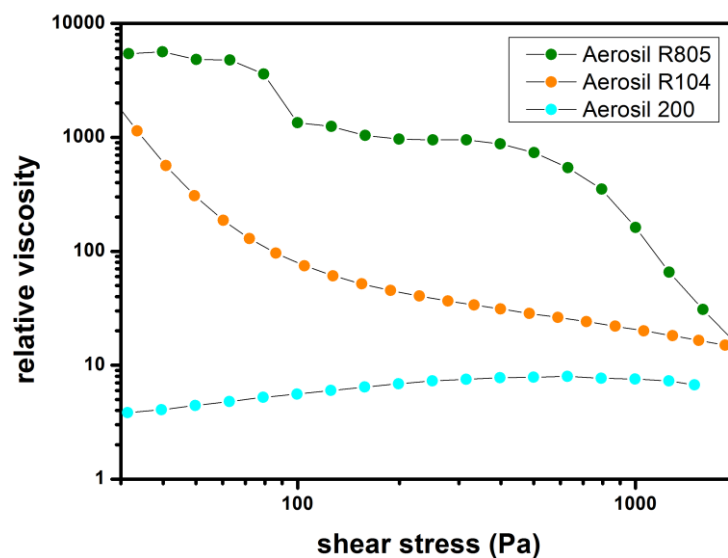


Figure B.4: Steady state flow curves of silica particle suspensions with various surface chemical in $[C_4mim][BF_4]$ with 10 wt% particle content.

Table B.4: Yield stress of 10 wt% suspensions of hydrophilic (Aerosil 200) and hydrophobic silica particle (Aerosil R104, R805) in $[C_4mim][BF_4]$

	Aerosil 200	Aerosil R104	Aerosil R805
Yield stress(Pa)	1.6 ± 0.2	2.3 ± 0.2	3.4 ± 0.5

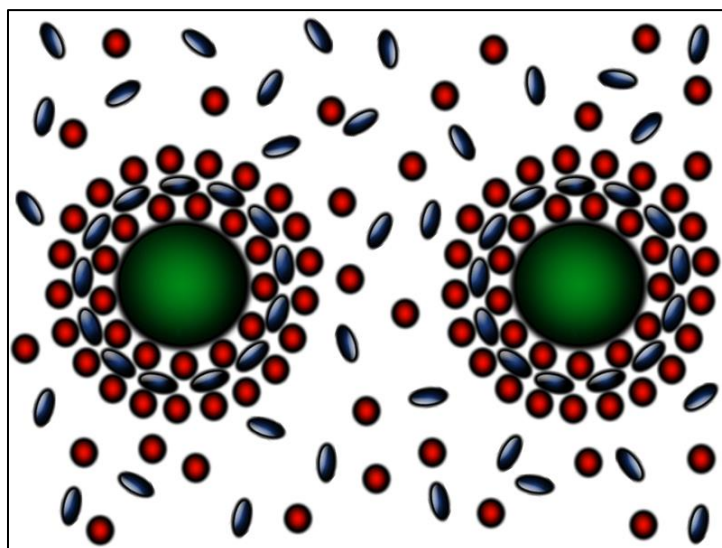


Figure B.5: Schematic illustration of hydrophilic Aerosil particles stabilization in $[C_4mim][BF_4]$ by solvation layer.

B.3 Conclusions

In this work, shear thickening fluids (STFs) suspensions in an ionic liquid are successfully formulated using a variety of silica based colloidal particles. The preparation protocols for the suspensions have been systematically studied and have confirmed that the BeadBeater mixer probably produces the desired STF suspensions with respect to the efficiency and reproducibility. Several factors (*e.g.*, particle size, surface chemical, hydrophobicity) have been investigated on fumed amorphous silica particle systems. It is found that Aerosil hydrophilic particles show similar critical

shear stress dependence on particle size as for the hard sphere silica particles. Hydrophilic Aerosil silica particles are able to be well dispersed and stabilized in [C₄mim][BF₄] exhibiting shear thickening behavior due to the solvation layering structure induced by hydrogen bonding. Whereas, hydrophobic Aerosil silica particles failed to form homogenous suspensions due to the absence of solvation layers and show shear thinning behavior because of the breaking of agglomerate secondary structure under shear.

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