Ionic Liquid as Surfactant in Pickering Emulsions Stabilised by Silica Particles

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Publications and Conferences

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Abstract

Investigations were carried out on the use of ionic liquid as an adsorbing surfactant in Pickering emulsions stabilised by silica particles. Colloidal silica nanoparticles, Ludox CL (positively charged) and Ludox HS-30 (negatively charged), and 2 μm silica particles were used for both the aqueous dispersion studies in ionic liquid and emulsion studies.

Ludox CL and Ludox HS-30 dispersions in aqueous 1-ethyl-3-methylimidazolium tetrafluoroborate ionic liquid (IL) was studied. Ludox HS-30 formed stable, less turbid dispersions while Ludox CL formed unstable, more turbid dispersions with sedimentation at higher IL concentrations.

Dynamic light scattering was used to characterize both Ludox CL and Ludox HS-30 dispersions. The results showed that as the IL concentration increased, the zeta potential values for Ludox CL changed from +34 mV to reduced negative values while zeta potential values for Ludox HS-30 shifted from -30 mV to lower negative values. The particle size increased with increasing IL concentration in both Ludox CL and Ludox HS-30, indicating particle aggregation and decreased dispersion stability.

Emulsions studies with silica particles and octane was done at octane to water volume ratio of 1:1. Ludox HS-30 formed stable oil-in-water (o/w) emulsions at intermediate IL concentrations ranging from 2.5×10^{-2} M to 2.0×10^{-1} M, while Ludox CL formed unstable o/w emulsions at all the IL concentrations investigated.

For investigations with micron-sized silica particles, stable o/w emulsions were formed at IL concentrations from 3.9×10^{-4} M to 5.0×10^{-2} M for both the powdered particle method and when particles were originally dispersed in octane. However, when particles were initially dispersed in water, no stable o/w emulsions were observed except at IL concentration of 5.0×10^{-2} M.

More stable o/w emulsions were obtained by keeping the IL concentration constant at 1.56×10^{-3} M than at 1.25×10^{-2} M while varying the particle concentration.

The results indicate that the IL was acting as an adsorbing surfactant in Pickering emulsions with Ludox HS-30, micro-sized silica particles originally dispersed in octane and the powdered particles method but could not effectively act as a surfactant when the micron-sized silica particles were initially dispersed in water.

Contents

Chapter 1 Introduction

1.0 Background

This chapter contains the introduction and literature review of this thesis. It explains in details, the definitions, types, principles and applications of the key terms used in this research; such as surfactants, ionic liquids, emulsions and silica particles. The explanations are supported with relevant literatures. The aims and objectives of the research are also captured.

1.1 Surfactants

1.1.1 Definition

A surfactant or surface-active agent [1-6] is a substance that lowers the surface tension of a liquid while increasing the wetting and spreading capabilities of the liquid. Surfactants function as emulsifying, foaming or dispersing agents by congregating at the interfaces between various substances.[1-6] They are found in many different goods including detergents. With hydrophilic "heads" and hydrophobic "tails," the majority of surfactants reduce surface tension when a liquid comes into contact with another phase, be it liquid, solid or gas. Surfactant has also been defined as an organic compound which contains at least a solvent-loving group (lyophilic) and a solvent-fearing group (lyophobic) in its molecule, [7] which is responsible for the surface activity exhibited. Hence, a surfactant molecule is amphiphilic in nature. The amphiphilic feature of a surfactant is largely responsible for their ability to exhibit surface activity and adsorb at interfaces thereby substantially changing the physical properties at those interfaces. They can also aggregate in bulk.[2, 7-9] Figure 1.1(a) is the schematic of a surfactant molecule, showing the polar head and the non-polar tail while (b)[10] shows the area the tail and the head group of a surfactant molecule subtend at an oil/water interface. Structure (b) is from ref.[10]

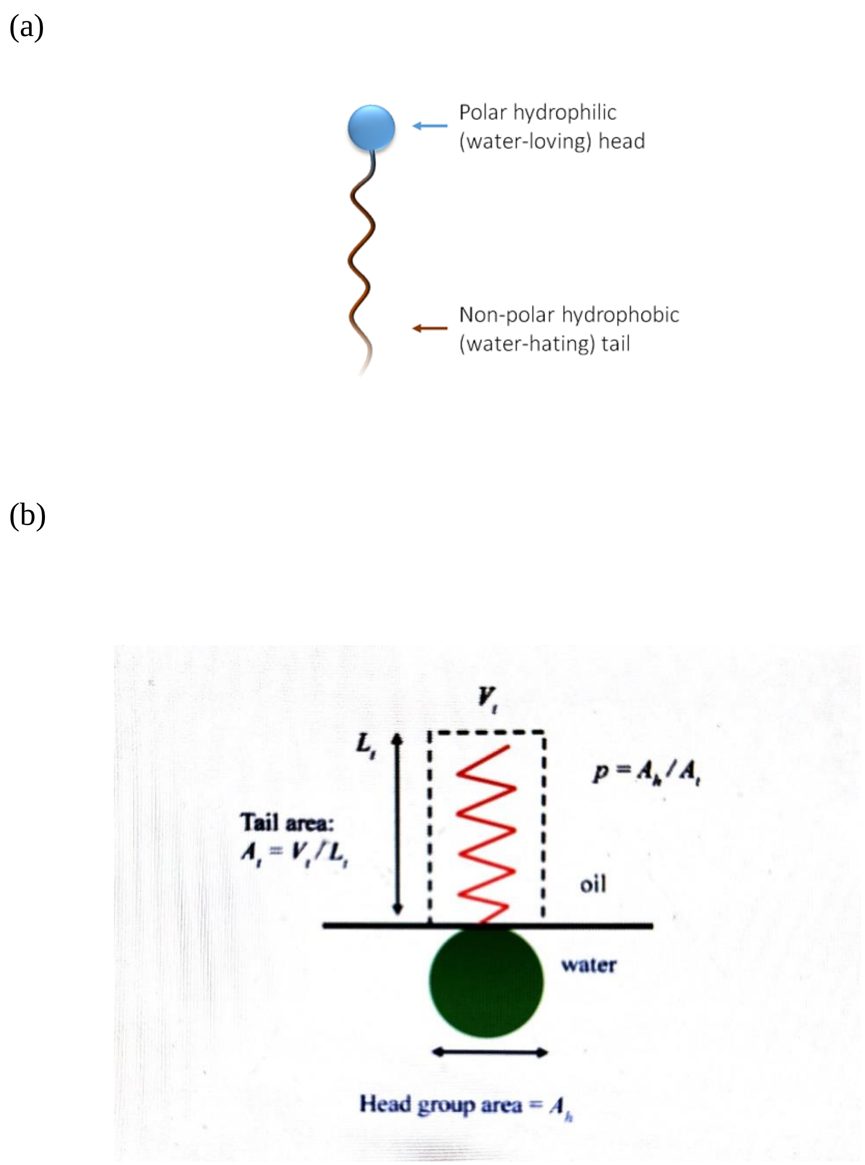


Figure 1.1 Schematic of a surfactant molecule showing

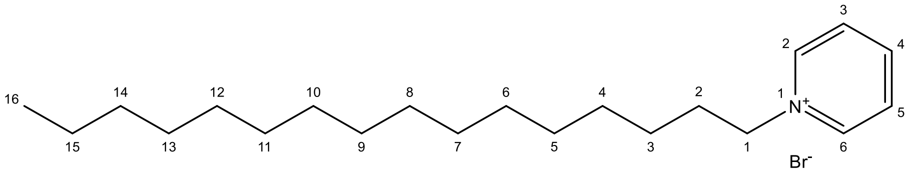
(a) the polar head and the non-polar tail, (b) the area that the head-group and tail of a surfactant molecule subtends at an oil/water interface from ref [10].

1.1.2 Types of surfactant

Surfactants are categorized into different groups according to their usage, charge and chemical structure.

Cationic Surfactants

These are surfactants whose hydrophilic heads are positively charged such as trimethylammonium ion ($-N(CH_3)_3^+$). Generally, they have a low critical micelle concentration (CMC) that allows them to form micelles in solution at comparatively low concentrations. They are distinguished by their ability to adsorb *via* electrostatic interactions onto negatively charged surfaces, such as hair, metal, plastic, solid particles or interfaces. Cationic surfactants are used in many different industrial applications in household goods, textiles, personal care and pharmaceuticals as hair conditioners, fabric softeners, germicidal or antiseptic properties and in formulations for monitored release of medications. Some examples of cationic surfactants include hexadecylpyridinium bromide, *n*-didodecyldimethylammonium bromide (DDAB) and dehydrogenated tallow dimethyl ammonium chloride.[4, 8, 9, 11] The structure of hexadecylpyridinium bromide is shown in Figure 1.2.

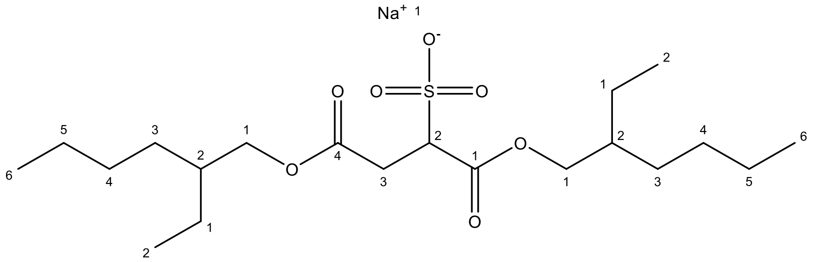


hexadecylpyridinium bromide

Figure 1.2 Structure of a cationic surfactant, hexadecylpyridinium bromide.

Anionic Surfactants

The hydrophilic head of these surfactants is negatively charged. Sulfates ($-OSO_3^-$), sulfonates ($-SO_3^-$), and carboxylates ($-CO_2^-$) are some examples of anionic surfactants. Anionic surfactants are soluble in aqueous solution due to the ionic interactions that their negatively charged head creates with water molecules. In addition to their good spreading and wetting abilities, anionic surfactants have high foaming properties and are used in production of detergents, cleansing and dishwashing liquids and together with cationic surfactants as a mixed surfactant blend. Sodium bis(2-ethylhexyl)sulfosuccinate (Aerosol-OT) is an example of an anionic surfactant and is shown in Figure 1.3.[8, 12, 13]



Sodium bis(2-ethylhexyl) sulfosuccinate

Figure 1.3 Structure of an anionic surfactant.

Nonionic Surfactants

These are surfactants whose hydrophilic heads are uncharged. However, they contain polar functional groups with strong affinity for water such as ether which makes them form hydrogen bonds. Most non-ionic surfactants are useful in various industrial processes because they are stable at high temperatures as well as across a broad temperature range. They have reduced sensitivity to hardness of water, decreased foaming ability compared with anionic surfactants and can be used together with both anionic and cationic surfactants. Their applications include pharmaceuticals and personal hygiene products. Alcohol ethoxylates, nonylphenoxy polyethylenoxy alcohols, Triton X-100 and ethylene oxide/propylene oxide block copolymers are some examples of non-ionic surfactants.[8, 13, 14] Figure 1.4 is a structure of Triton X-100.

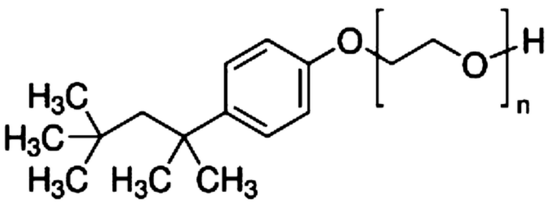


Figure 1.4 Structure of a poly (ethylene glycol) derivative, Triton X-100, a non-ionic surfactant (where n has a value from 9 to 10).

Zwitterionic Surfactants

They possess positively and negatively charged groups in their structure and can display a different charge, ranging from negative to neutral to positive. Zwitterionic surfactants are adaptable in both acidic and alkaline circumstances due to their ability to operate well in a broad variety of pH situations. Due to their mild nature, they are a good choice for personal care products that aim to reduce irritation of the skin and eyes. They can function as buffers in some formulations helping to stabilize pH levels because of their amphiphilic nature. Complex systems can be formed by amphoteric surfactants because they are frequently compatible with non-ionic, anionic and cationic surfactants. An example of a zwitterionic surfactant is a cetyl betaine (CH3(CH2)15N+(CH3)2CH2COO−), shown in Figure 1.5. [8, 15]

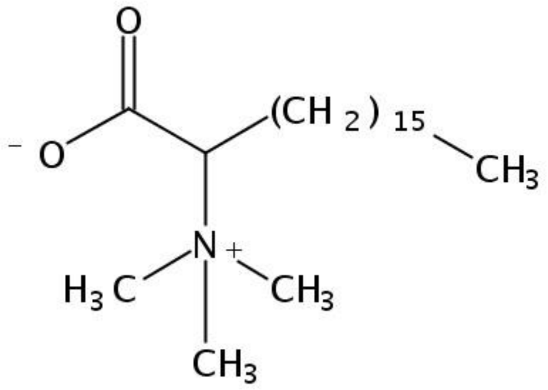


Figure 1.5 Structure of a zwitterionic surfactant, cetyl betaine.

1.1.3 Surfactant behaviour in water

Surfactants display several properties because of their special structure and surface activity. Surfactants can reduce the surface tension of liquids, which makes them advantageous for a variety of processes like foaming, detergency and emulsification. This is a summary of how surfactants behave in water:

i. **Solubilisation and solubility:** Solubilisation is when an insoluble substance is made to dissolve in a particular medium.[2] It involves solubilizing a poorly water-soluble material with surface-active chemicals to increase its solubility. Surfactants are surface-active agents, hence are able to dissolve both polar and non-polar substances through the formation of micelles.[2, 7, 11, 16-18]

ii. **Formation of micelle:** Micelles are aggregates made up of surfactant molecules, and entail exposing the hydrophilic heads to water and protecting the hydrophobic tails from water. [2, 9] The formation of micelles is known as micellisation and the critical micelle concentration (CMC) is the particular surfactant concentration at which micellisation occurs. When concentrations are higher than the CMC, there is no obvious difference in the surfactant qualities of the solution as the monolayer concentration remains largely unchanged and uniform.[9, 12] consequently, if the concentration of the surfactant increases, it alters the structure of the micelles change if there is a rise in the surfactant concentration. At room temperature, the normal CMC values for the major types of surfactants are 10^{-3} to 10^{-1} M for cationic and amphoteric surfactants, 10^{-3} to 10^{-2} M for anionic surfactants and 10^{-5} to 10^{-4} M for non-ionic surfactants. [9, 12]

iii. **Wetting:** The readiness of a liquid to spread across a solid surface is referred to as wetting.[2, 19] Surfactants are essential for altering and regulating wetting features. Surfactants encourage liquids to permeate or spread across a surface and facilitate the liquid's interaction with the surface because of their dual properties. Hence, surfactants can adsorb at interfaces and change the surface tension and wetting behaviour at interfaces.[2, 19, 20] Wetting is measured by the contact angle that forms at the solid-liquid interface. By adsorbing at the interface and modifying the balance of forces between the liquid and solid phases, surfactants can change the contact angle.[21] This measurement is frequently used to describe how liquids and solids interact as well as the wetting characteristics of surfaces. It is the tangent to the three-phase contact line where solid, liquid, and vapour intersect.[20, 21]

iv. **Emulsification/demulsification:** Surfactants can disperse solid particles in a liquid to enhance the stability of the dispersion, or they can disperse one liquid into another immiscible liquid to produce an emulsion. By creating a barrier around tiny droplets of one liquid distributed in a second immiscible liquid, surfactants stabilize emulsions.[22]

1.2 Ionic liquids

1.2.1 Definition, properties and applications

Ionic liquid has been an area of increasing research interest after it was first discovered by Walden[23, 24] in 1914. Room temperature ionic liquids are a particular class of salts which exist as molten salts and liquids at comparatively low temperatures that is mostly below 100 °C. Hence the age-long definition of ionic liquids as salts with melting points below 100 ^{o}C [25, 26] , a definition that is fast becoming impracticable because of some conventional solvents with low melting points and the application of surface-active ionic liquids in water.[25, 27] Ionic liquids are made mostly of ions and comprised of organic cations and inorganic or organic anions. The major difference between ionic liquid and traditional molten salts is that the former contains organic cations while the later contains inorganic cations. [25, 26]

Unlike conventional solvents, ionic liquids also have corresponding weaker interactions like π-stacking and H-bonding as well as their ionic and covalent bonding. [28, 29] Ionic liquids have broad underlying characteristics that are tunable and can be adjusted to match diverse needs and the availability of many cations and anions gives room for a widespread of possible ionic liquids, hence they are special and adaptable for a variety of applications.[25, 28]

Room temperature ionic liquids contain huge lopsided organic cations like phosphonium, imidazolium, quaternary ammonium, and pyridinium combined with different anions like hexafluorophosphate $[PF_6]^-$, tetrafluoroborate $[BF_4]^-$, halides (Cl^-, Br^-, I^-), [25, 28] *etc*. Imidazolium-based ionic liquids are among the most researched class of ionic liquids, with studies showing that altering the length of the imidazolium alkyl chain changes the physical properties of the ionic liquid significantly.[25, 28]

1.2.2 General properties of ionic liquids

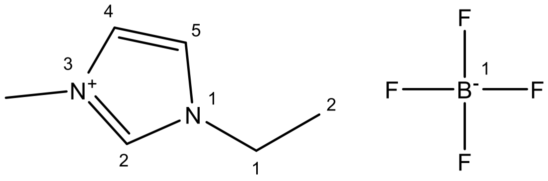
Reduced vapour pressure/low volatility: Ionic liquids have negligible vapour pressure and are non-volatile, hence they are incombustible unlike conventional molecular solvents. This feature decreases the chance of exposure to dangerous vapours because they cannot emit volatile organic compounds, therefore promoting industrial and environmental safety.[25, 30-34]

Low melting point and wide liquidus range: Some ionic liquids have melting points as low as -100 °C. The large and asymmetrical feature of the constituent anion and cation of the ionic liquid lowers the lattice energy of the crystalline form leading to low melting point.[25, 26, 30, 31, 35, 36] The range of temperature between the freezing point and the boiling point is about 459 °C for ionic liquids. This is wide compared to 100 °C for water and about 75 °C to 200 °C for most conventional solvents.[37, 38] This broad liquidus range and the high thermal and chemical stability of ionic liquids make them suitable as heat transfer fluids. They are more resilient and appropriate for uses where conventional solvents would break down.[31, 32, 39]

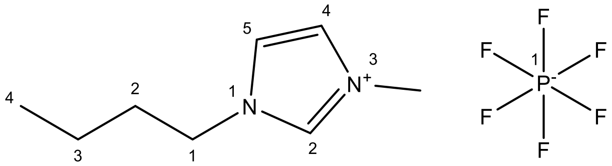
Wider solubility range than normal molecular solvents: Room temperature ionic liquids have a broad range of solubility which enables them to dissolve a vast range of molecules, both polar and non-polar. This helps their application in extraction, separation and product recovery processes.[25, 40-42].

Density and viscosity: Ionic liquids also have higher densities and viscosity compared to conventional solvents [25, 43-45] and varied conductivity.[46, 47]

All these unique properties [25, 48-50] of ionic liquids gained them the “green solvents” title and gave them preference over conventional solvents in several applications.[33, 51-54] Some studies show that they still exhibit some toxicity and biodegradable challenges despite being referred to as green solvents. [50] Examples of imidazolium based ionic liquids are shown in Figure 1.6.



1-ethyl-3-methylimidazoliumtetrafluoroborate



1-butyl-3-methylimidazolium hexafluorophosphate

Figure 1.6 Examples of imidazolium-based ionic liquids.

1.2.3 Ionic liquids as surfactants

Among the numerous applications of room temperature ionic liquids is their use as surfactants. [55] Ionic liquids can function as surfactant in a variety of applications. They have surface-active qualities such as the presence of long aliphatic chains that make them useful for improving interfacial characteristics, stabilizing emulsions and influencing aggregation at surfaces.[27] Both room temperature ionic liquids and ionic liquid-based surfactants have shown to offer potential in a number of fields and applications, including chemical synthesis, catalysis, emulsification, separation procedures and oil recovery in the petroleum sector.[27, 56-60]

Features of ionic liquids as surfactants

Room temperature ionic liquids and ionic liquid-based surfactants have a number of characteristics that make them suitable to be used as surfactants. Here are some of the features:

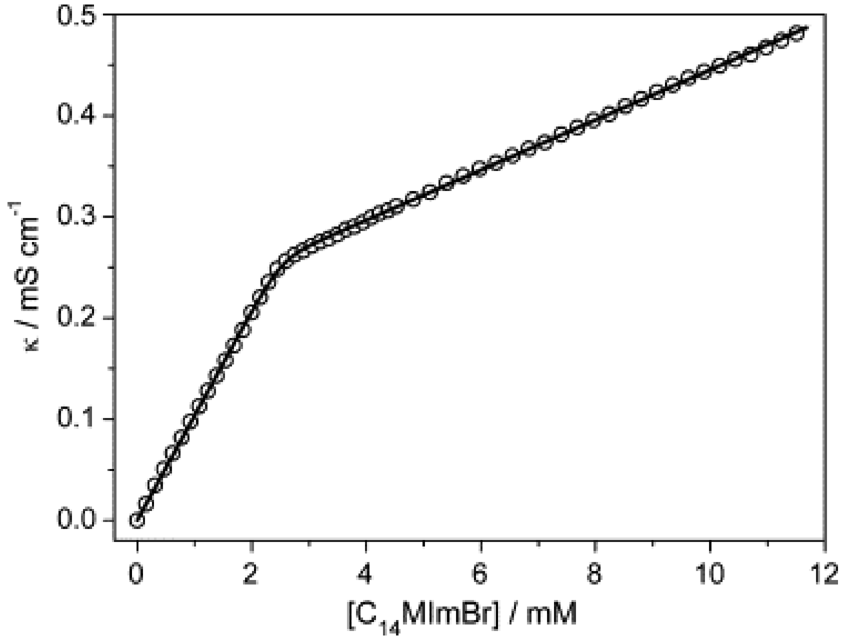
Adaptable surface-active characteristics: They are well-known for their adaptable surface-active characteristics which enhance performance in a range of applications. They have increased surface activity and the ability to produce micellar solutions.[27, 61]

Strong influence on interfacial adsorption and aggregation: They have a positive effect on aggregation at interfaces and interfacial adsorption, which is useful for emulsion stabilization and interfacial aggregation. They achieve this by keeping their hydrophilic part in the polar phase while the hydrophobic region stays adjacent to the less polar phase, thereby decreasing the interfacial forces and interfacial tension.[60, 62]

Self-aggregation ability: Like conventional surfactants, they possess this crucial property to self-aggregate which enables them to form micelles in aqueous and mixed solutions over the critical micelle concentration. This is key for its role in emulsion stabilization and other applications. [61]

Colloidal aggregation in water: Ionic liquid-based surfactants have long hydrophobic “tails” and can lower the surface tension and form colloidal aggregates such as micelles and vesicles in water, [63-68] making them worthy to be used in many systems and processes.[58] Vanyur et al [65] demonstrated the better formation of micelles in aqueous medium by ionic liquids. They measured and compared the conductivity and fluorescent probes of alkyltrimethylammonium bromides surfactants and 1-alkyl-3-methylimidazolium bromide (CnMImBr) ionic liquids. The results show a linear relationship between the critical micelle concentration (cmc) logarithm and the number of carbon atoms in the hydrocarbon moiety of the ionic liquids, with the cmc of the ionic liquids being obviously lower than those of the corresponding surfactants. The data is shown in Figure 1.7. from ref. 65. [65] This affirms the ability of ionic liquids to form micelles in aqueous solution at a more favourable energy than surfactants.

a.



b.

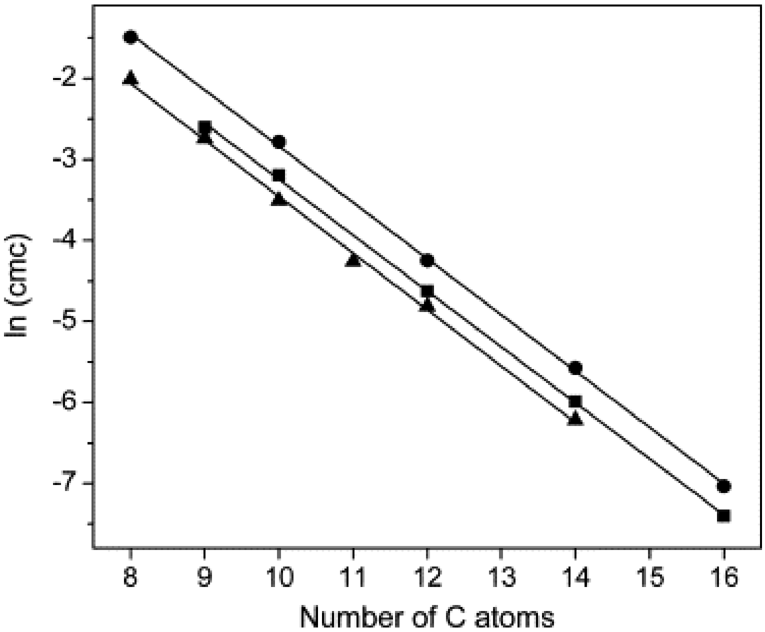


Figure 1.7 (a) Effect of the variation of C14MImBr concentration on the specific conductivity in aqueous solution at 298K; (b) Logarithm of the cmc as a function of the number of carbon chain for the surfactants (circles), the ionic liquids (squares) and the sulphates (triangles).

Some ionic liquids with surface activity comprising 1-alkyl-3-methylimidazolium cation were shown to surpass conventional ionic surfactants in their ability to reduce surface tension and form micelles in water. This was demonstrated by Dong et al [64] in their research data in Figure 1.8.[64]

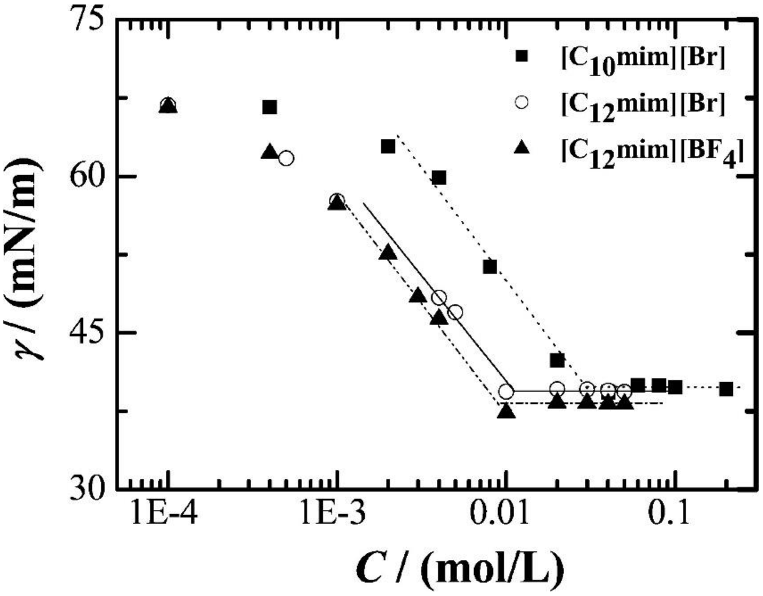


Figure 1.8 Surface tension versus concentration of ILs at 298. Key: [C_{10}mim][Br] (▪); [C_{12}mim][Br] (○); [C_{12}mim][BF_4] (▲). [64] (where mim is 3-methylimidazolium).

1.3 Emulsions

1.3.1 Definition and types of emulsions

An emulsion is a heterogeneous dispersion composed of two immiscible liquids, with one of the liquids being dispersed as droplets within the other.[5, 10, 19, 69-72] An emulsion consists of two primary phases: the dispersed phase and the continuous phase. The liquid droplets form the dispersed phase while the continuous phase is the medium in which they are dispersed. Emulsions are commonly seen in products like food, cosmetics, and pharmaceuticals. Everyday examples of emulsions are milk, butter, cream, cheese, salad dressings, homogenized milk, mayonnaise and various skincare products.[5, 19]

Emulsions are grouped into various types according to the composition of the dispersed and continuous phases. They can be simple or multiple emulsions.[2, 10, 73-75]

Oil-in-water (o/w) emulsion: This is the dispersal of oil droplets in water. The dispersed phase is the oil while the continuous phase is water.

Water-in-oil (w/o) emulsion: In this water droplets are dispersed in oil, where oil is continuous phase and water the dispersed phase. O/w and w/o are simple emulsions.[2, 10]

Multiple (double) emulsions: These are complex emulsions that contain both water-in-oil (w/o) and oil-in-water (o/w) and emulsions, which have multiple phases. Multiple emulsions are composed of droplets within droplets spread in a continuous phase. They comprise water-in-oil-in-water (w/o/w) and oil-in-water-in-oil (o/w/o) emulsions.[2, 73-75]

Figure 1.9 is a schematic diagram of both simple and multiple emulsions. The emulsion type formed can be ascertained through the drop test.[76, 77] This involves adding the emulsion drop to some volume of either the dispersed phase or the continuous phase. o/w emulsion will disperse in water whilst w/o emulsion will disperse in oil.

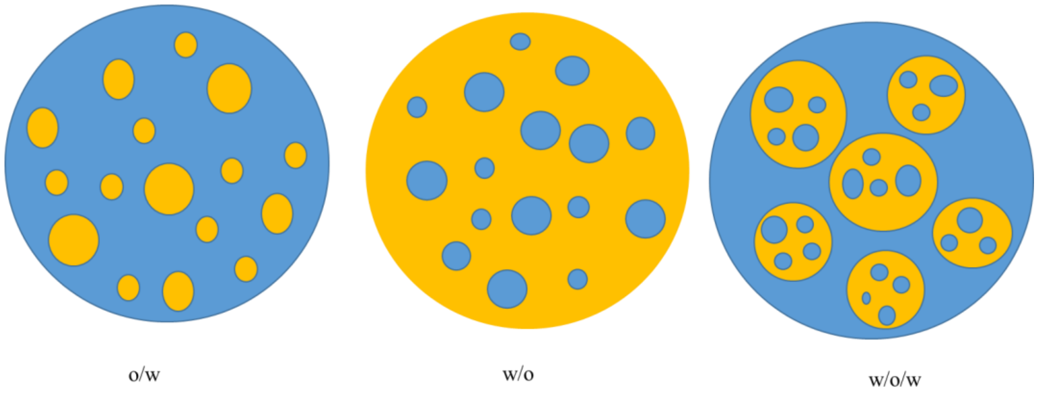


Figure 1.9 Schematic of simple and multiple emulsions in oil+water mixture.

In terms of the free energy (ΔG) of formation shown in equation 1.1 [10], an emulsion is unstable thermodynamically [10, 78] without an emulsifier because the presence of the dispersed droplets raises the interfacial area (ΔAγ) across the two immiscible liquids involved.[78] This makes ΔG to be positive leading to immediate complete phase separation of the emulsion formed. The largely increased interfacial area makes the value of the change in entropy (TΔS) to be really negligible.[78] However, in microemulsions, when an emulsifier is added either as a surfactant or solid particle, it greatly decreases the interfacial tension reducing the emulsification free energy thereby making ΔG negative and giving rise to making a stable emulsion.

$$\Delta G = \Delta A\gamma - T\Delta S \qquad (1.1)$$

1.3.2 Emulsion stability and breakdown processes

Emulsion stability is the capacity of an emulsion to withstand breakdown.[10] It is a kinetic notion in which there is no visible change in size, quantity and placement of the emulsion droplets all through the timeframe of the experiment.[70] The following breakdown processes occur in emulsions:

(a) Sedimentation (creaming):

Sedimentation and creaming are two equivalent processes that occur in a w/o and o/w emulsion systems respectively as a result of buoyancy caused by the difference in the densities of the two phases. It hardly affects the spread of the droplet size. Sedimentation occurs when denser water droplets sit at the bottom of the system in a w/o emulsion while creaming is the process whereby less dense oil droplets float in an o/w emulsion.[2, 10, 19, 70] Creaming is reversible because tender shaking can take the emulsion droplets back to their initial steady distribution.[70]

Sedimentation (or creaming) of an isolated emulsion droplet is given by Stokes' law in which the velocity (v_s) is given in equation 1.2.

$$\upsilon_S = \frac{2r^2\Delta\rho g}{9\eta_0} \qquad (1.2)$$

where η_0 is the viscosity of the continuous phase, $\Delta\rho$ is the difference in the densities of the continuous and dispersed phase, g is the acceleration due to gravity and the radius of the droplet is r. [10]

Equation 1.2 shows that increasing the viscosity of the continuous phase, decreasing the density difference or reducing the size of the droplets can reduce sedimentation (or creaming) in emulsions.[10, 19, 70]

(b) Coalescence:

This happens when two or more emulsion droplets combine to form a single droplet with smaller interfacial area but larger volume.[2, 70] During coalescence, there is the breaking of the film of continuous phase between the droplets because of the effect of van der Waals force of attraction. This results in a permanent and irreversible fusion of the droplets.[10, 19, 70] Continuous coalescence leads to the two integral liquids in the emulsion undergoing a complete phase separation.[10] However, the presence of stabilisers like nanoparticles and surfactants at the interface slows down coalescence.[10]

(c) Flocculation:

Flocculation is the aggregation of individual droplets of emulsion to form a loose gathering of droplets with each droplet retaining its identity. Unlike coalescence, flocculation does not rupture the film of continuous phase connecting the droplets. Consequently, flocculation can be partly reversible.[2, 19, 70]

(d) Ostwald ripening:

Ostwald ripening is when large droplets get bigger at the cost of tinier droplets as a result of the variance in the chemical potential and solubility between the molecules in the smaller and larger droplets.[2, 70] Ostwald ripening thrives with the difference in pressure, ΔP, within and outside the droplet and is explained by the Laplace equation 1.3:

$$\Delta P = \frac{2\gamma}{r} \qquad (1.3)$$

where ΔP is the pressure difference and the radius of the droplet is r.[2, 10]

The effect of the radius of the droplet can be seen using the Kelvin equation and solubility shown in equation 1.4.[2]

$$Ln(S_1/S_2) = \gamma_i V/RT(1/r_1 - 1/r_2) \qquad (1.4)$$

where V is the molar volume of the droplet phase, the solubilities of the droplets are S_1 and S_2 with radii r_1 and r_2 respectively.[2]

A schematic of the different breakdown processes in an emulsion is shown in Figure 1.10 redrawn from refs.[2, 19, 79]

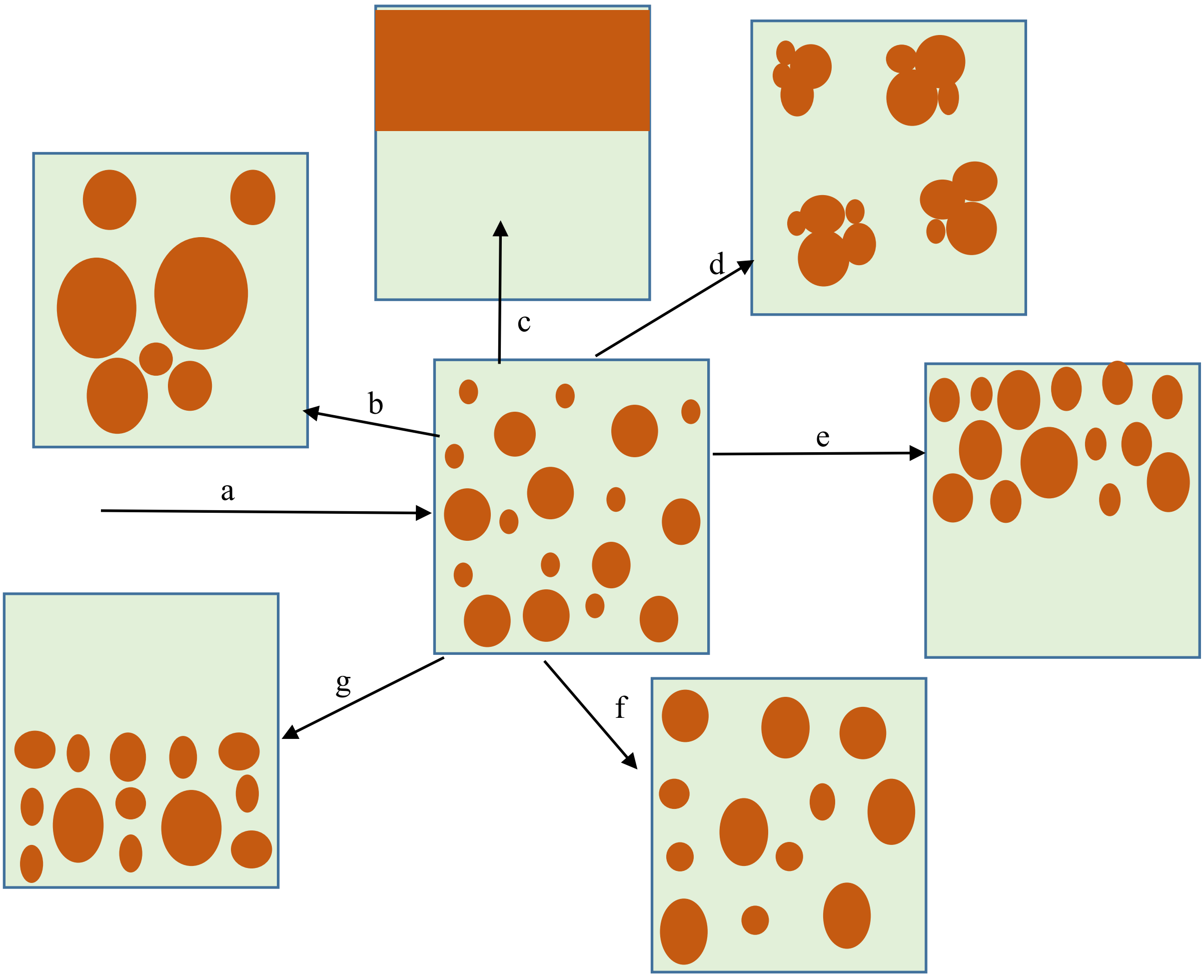


Figure 1.10 Schematic of emulsion breaking processes. **a** is original emulsion, **b** is coalescence, **c** is breaking (complete phase separation), **d** is flocculation, **e** is creaming, **f** is Ostwald ripening and **g** is sedimentation.

An emulsifying agent or emulsifier stabilizes emulsions by preventing droplets from aggregating and separating. The stability of emulsions is significant in emulsion composition and application. Stable emulsions are resistant to demulsification and can last for weeks or even years. On the other hand, emulsifying agents like surfactants and small solid particles make up the majority of metastable emulsions. These emulsifying agents facilitate the formation and stability of emulsions.[5, 71]

1.3.3 Introduction to Pickering emulsions

Pickering emulsions are emulsions stabilized by solid particles.[10, 71, 74] The particles adsorb at the interface of the two immiscible liquids, such as oil and water, as opposed to traditional emulsions stabilized by surfactants or other emulsifying agents.[80]

Pickering emulsions were accredited to Pickering[81] when his earliest work was published in this area in 1907. He referred to a similar work by Ramsden[82] four years earlier, where protein solid particles were used to stabilise foams. Pickering emulsions have rheological properties which can be adjusted for particular applications and uses. The applications of Pickering emulsions have been investigated over the years, with a significant increase in the past decade. Pickering emulsions have outstanding biocompatibility which enhances their application in the food [83] and health sectors as nanostructured lipid carriers and probiotics encapsulation.[84] Other applications include 3D printing,[85] pollution control and waste water treatment,[86] drug delivery, increased shelf life of agricultural products [87] and oil drilling among others.

1.3.4 Adsorption of particles at oil-water interfaces

Particles free energy at the oil-water interface

The shape of a small spherical particle adsorbing at oil-water interface can be regarded as planar at the contact surface and the minimum energy required to detach such a particle from the oil-water interface is given in equation 1.5 below .[88]

$\Delta G_d = \pi r^2 \gamma_{ow}(1 \pm cos\theta)^2$ (1.5)

Where ΔG_d is the free energy of detachment and θ is the three-phase contact angle, which is "+" for hydrophobic particles ($\theta > 90^o$) and "−" for hydrophilic particles ($\theta < 90^o$).[88]

The effect of the contact angle on the free energy of detachment (ΔG_d) is shown in Figure 1.10 for a spherical particle with radius (r) = 10nm and oil-water interfacial tension (γ_{ow}) = 50 mN m^{-1}

Figure 1.11 shows a progressive increase in the free energy of detachment ΔG_d from zero at contact angle $\theta = 0^o$ to a maximum at $\theta = 90^o$, and a steady decrease to zero at $\theta = 180^o$. At contact angles close to 90^o, nanoparticles exhibit irreversible attachment at the oil-water interface because their detachment energy is much greater than the thermal energy, kT (where T is the temperature, k = Boltzmann constant, ΔG_{do} = free energy of detachment into oil and ΔG_{dw} = free energy of detachment into water). This is unlike surfactants, which can easily attach and detach.[88]

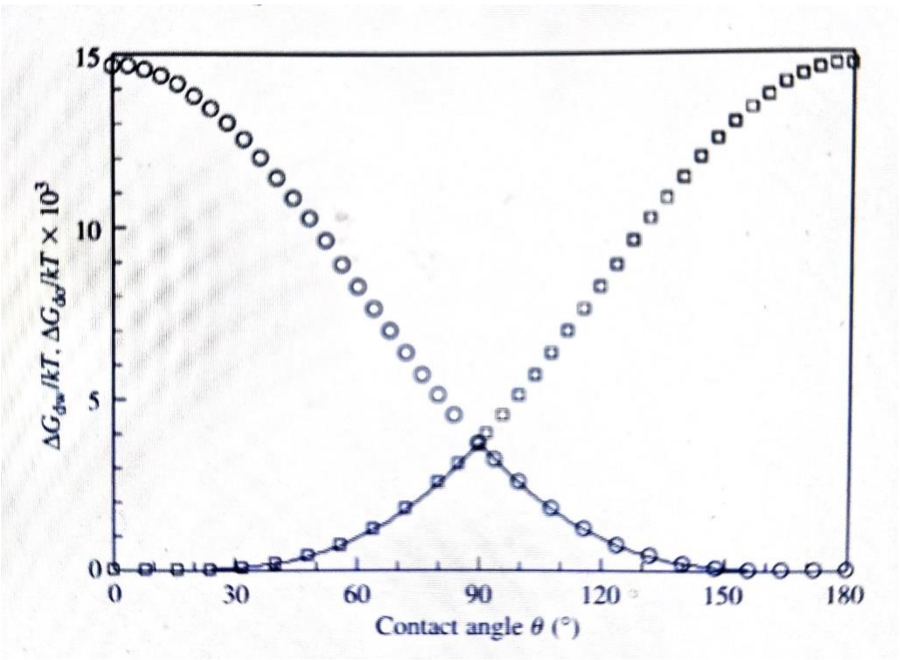


Figure 1.11 Energy of detachment (ΔG_d) of a spherical particle radius (r) = 10nm and oil-water interfacial tension (γ_{ow}) = 50 mN m^{-1} as a function of particle contact angleθ. Taken from ref 88.

Particles interactions at oil-water interfaces

Typical characteristics of particles include:

Stabilisation by solid particles: Solid particles, such as colloidal particles or nanoparticles, serve as stabilizers in Pickering emulsions. These particles can be inorganic like silica or clay or organic like polymer particles.[80, 89, 90]

Binks *et al.* in their work on the properties and preparation of emulsions solely stabilized by colloidal particles compared the behaviour of particle-stabilised emulsions with surfactant-stabilised emulsions. They reported maximum stability for some emulsions stabilized by solid particles at contact angles between 50 and 130^o at the oil-water interface, in contrast to emulsions stabilized by surfactants which are rather in quick dynamic equilibrium between the bulk phase and the oil-water interface. [91]

Adsorption at the oil-water interface: The ability of the particles to be wetted by the two liquids involved is the major driving force for the adsorption of the particles at the interface. Eventually, the particles will prefer one of the liquids over the other, causing the interface to curve in the direction of the less preferred liquid, thereby emulsifying it into droplets.[92] The wettability of the particles in the liquids, through the contact angle, determines if the emulsion will be o/w or w/o.[92] The contact angle represents the angle a liquid subtends at the three-phase line of contact where the solid, liquid and gas meet. [20, 88]

The contact angle is designated by Young's equation:

$$\mathrm{Cos}\theta = \frac{\gamma_{po}-\gamma_{pw}}{\gamma_{ow}} \qquad (1.6)$$

where γ_{ow} is the oil-water interfacial tension, γ_{po} is the particle-oil interfacial tension and γ_{pw} is that at the particle-water interface. [88]

If both liquids wet the particles evenly, then we have: $\gamma_{po} = \gamma_{pw} = 90^o$. Otherwise, it is: $\gamma_{po} > \gamma_{pw}$ and $0\,^o \leq \theta < 90^o$ for hydrophilic particles, and $\gamma_{po} < \gamma_{pw}$ and $90^o < \theta \leq 180^o$ for hydrophobic particles. So, hydrophilic particles normally form o/w emulsions while hydrophobic particles are more inclined to form w/o emulsions.[20, 70, 88, 93]

Figure 1.12 [94] shows the position of the emulsifying particles (hydrophilic and hydrophobic) and the contact angles when wetted by the two liquid phases (oil and water).

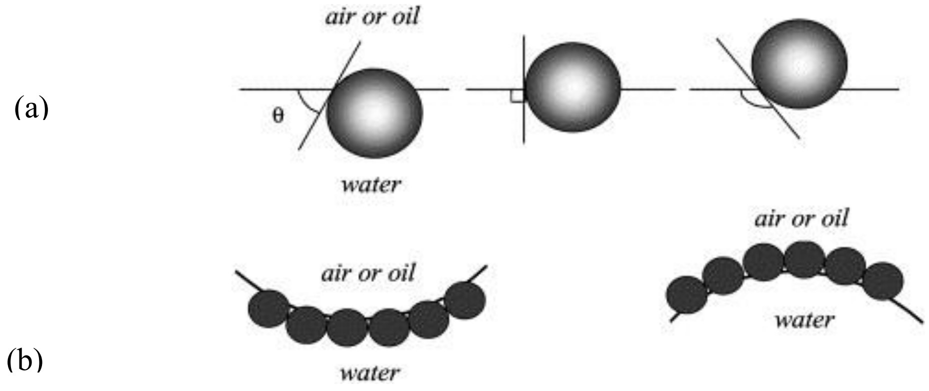


Figure 1.12 (a) Particles position at a planar oil-water interface for $\theta < 90^{\circ}$ (left), $\theta = 90^{\circ}$ (middle) and $\theta > 90^{\circ}$ (right). (b) Proposed particles position at a curved oil-water interface for hydrophilic (left) and hydrophobic (right) particles. Taken from ref. 94.

1.3.5 Pickering emulsions and stabilisation mechanisms

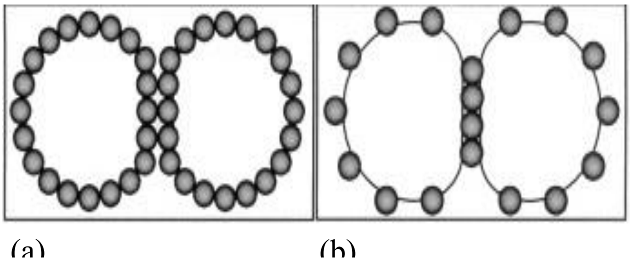
Pickering stabilisation occurs when solid particles sit at the interface of bubbles and droplets and resist the occurrence of emulsion breakdown processes such as Ostwald ripening and coalescence in an emulsion.[89]

Two stabilization mechanisms were proposed for emulsions stabilized by solid particles (Pickering emulsions). These are:

i. **Bilayer stabilisation:** This occurs when energy of adhesion wards off displacement from the interface.[78] Steric mechanism is favoured when the stabilizing solid particles efficiently and completely cover the emulsion droplets, forming a dense layer of particles around droplets, thereby resisting emulsion coalescence from occurring.[95-97]

ii. **Bridging monolayer mechanism:** This can happen when there is a low percentage of the particles covering the droplets and the scarcely populated stabilising solid particles form a bridge of monolayer around the droplets, hence preventing the coalescence of the emulsions.[96, 98, 99] Closeness to other particles stops lateral movement in this mechanism, thereby enhancing emulsion stability.[78]

Figure 1.13.[78, 96] is a schematic of these emulsion stabilisation mechanisms drawn from refs. 78 and 96.



(a) Steric bilayer
(b) Bridging monolayer

Figure 1.13 Pickering emulsion stabilisation mechanisms showing (a) steric bilayer stabilisation (b) bridging monolayer stabilisation.

1.3.6 Use of ionic liquids in Pickering emulsions

In the last two decades, there is a gradual but progressive shift from the use of conventional surfactants to ionic liquids as emulsifying agents in stabilizing emulsions. This is as a result of the many environmental and functional benefits of ionic liquids over conventional surfactants. The interaction of ionic liquids at liquid-liquid interfaces has been an area of great interest. This is because of the maximal tunable properties of ionic liquids and the countless ways of combining the cations and anions.[100]

Ionic liquids have been used in Pickering emulsions in mostly two ways. Firstly, to replace either oil or water and secondly to act as an emulsifier in an oil-water mixture to produce Pickering emulsions.

In Pickering emulsions, integrating particles into IL-liquid systems can lead to a lot of interesting possibilities with great applications in catalysis, extraction, reaction systems among others. [100-105]

In some of their early work, Binks *et al.* [106, 107] successfully prepared stable simple and multiple ionic liquid-based Pickering emulsions using some imidazolium-based room temperature ionic liquid and silica nanoparticles of about 20 nm as stabilisers. Different emulsion types and drop sizes, including phase inversion, were obtained by varying the percentage and wettability of the silica nanoparticles. Figure 1.14 [106] shows the phase inversion (dotted straight line) as a result of varying the wettability of the silica nanoparticles. Their results comprised simple, two component and three component multiple Pickering emulsions. The simple emulsions include oil-in-ionic liquid, ionic liquid-in-oil, water-in-ionic liquid and ionic liquid-in-water. However, the resultant particle arrangement could not be seen because of the tiny size of the silica nanoparticles used in the experiments, hence the inclusion of experiments using larger micron-sized silica particles in this research.

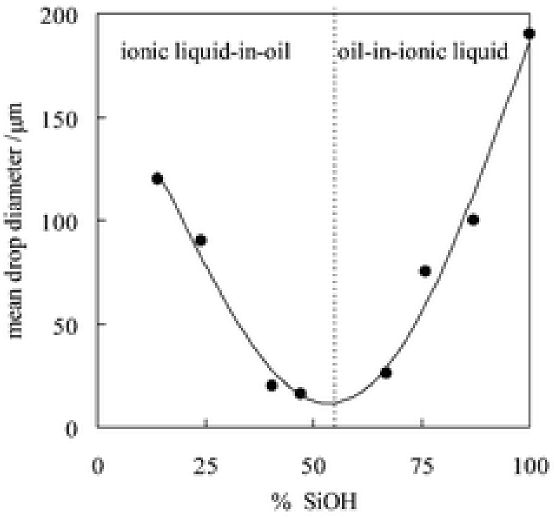


Figure 1.14 The mean drop diameter versus % SiOH of the silica particles for emulsions of Miglyol 810N and EmimBF in equal volumes and 1 wt% of silica particles from ref. [106]

Room temperature imidazolium-based ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF_6]), was used by Ma *et al* [108] in place of the droplet phase to generate an ionic liquid-in-water Pickering emulsion stabilised by treated polystyrene particles of size 1 to 1.1 µm. They compared the oil-in-water Pickering emulsions with the ionic liquid-in-water Pickering emulsions and observed that the droplets were well covered by the particles in the former while the later had droplets partly covered with the same particles. This observation suggests that the particles have more affinity for the ionic liquid-water interface than for the oil-water interface because the particles are positively charged and readily adsorb at the interface. Their findings also showed that the micron-sized particles did not just equilibrate at the ionic liquid-water interfaces but also showed a partitioning preference in the continuous and dispersed phases, with hydrophobic particles having a preference for the hydrophobic ionic liquid and the hydrophilic particles preferring the water phase, enhancing emulsion stability. [108] The microscopic images is shown in Figure 1.5.

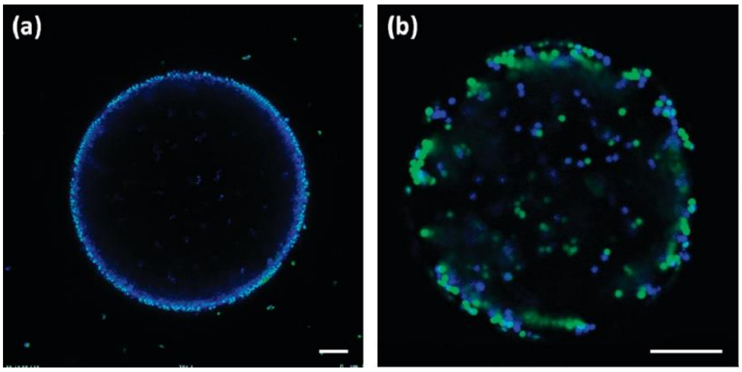


Figure 1.15 [108] Microscope images of a cross section of [BMIM][PF_6]. (a) The droplet interface is partly covered with the particles (b) The droplet interface is fully covered with particles and the concentration of particles is higher in the [BMIM][PF_6] phase as compared to the aqueous phase. The displayed scale bar is 10 µm. From ref. [108].

Nickerson *et al*. [100] used fluorescent micron-sized particles and the hydrophobic ionic liquid, [BMIM][PF_6] as the droplet phase, to successfully prepare ionic liquid-based Pickering emulsions that showed the resulting droplet arrangement and partition preferences of the particles. When the ionic liquid turned from being the droplet phase to the continuous phase, water-in-ionic liquid or oil-in-ionic liquid Pickering emulsions were prepared and particle bridging [109, 110] was observed.

In a more recent work, Xu et al [111] used both hydrophobic and hydrophilic ionic liquids to prepare Pickering emulsions, with heptane as oil and fumed hydrophobic silica as stabiliser. The research showed the formation of stable ionic liquid-in-hexane Pickering emulsion with about 40 % of the volume of the dispersed phase for [BMI][NTf_2] due to the irreversible adsorption of the silica particles around the ionic liquid/hexane interface. There was a reversal from simple to multiple hexane-ionic liquid-hexane emulsion when the volume fraction of the dispersed phase increases to 50 %. Figure 1.16 shows the optical microscopic images of both the simple and multiple emulsions formed from ref. 111.

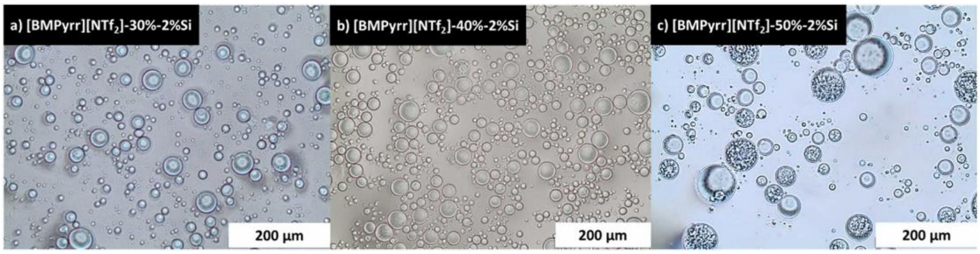


Figure 1.16 [111] Optical microscopy of [BMPyrr] [NTf_2]-Pickering emulsions stabilized by fumed silica (2%) with different dispersed volume fractions of ionic liquid; a) 30%, b) 40%, and c) 50%. From ref. [111].

1.4 Silica particles

Nanometer and micrometer-sized silica particles are found in a variety of forms and sizes. The properties and applications [112, 113] of silica is influenced by their size, shape and porosity. Silica has an estimated refractive index of 1.43 and a density of about 2 g/cm^3. Silica nanoparticles have a range of size from 1 to 100 nm. Their special properties, such as morphology, small range of pore sizes and big distinct surface area, are responsible for their vast applications as drug delivery channels, [114-119] catalyst carriers, solar cells, framework for nanoparticle growth among others.[120]

One of the best known properties of silica nanoparticles is its exceptional biocompatibility, little cytotoxicity and narrow distribution of controlled size.[121-124] With an empirical formula of SiO_2, silica is composed of silicon atoms and oxygen atoms in a 1:2 net ratio in both its crystalline and amorphous forms. In liquids, silica particles can disperse to create colloidal systems, which is crucial for applications like paints, coatings and inks.[125, 126]

Silica nanoparticles usually possess a high surface area because they are porous and have the ability to absorb and release gases and liquids. This feature makes them appropriate for use for advanced catalysis, adsorption, biomedical and drug delivery applications.[127, 128]

Silica particles also have a high degree of heat stability and are appropriate for use in high-temperature situations because they can withstand elevated temperatures without experiencing substantial structural changes.[129, 130] Silica resists deterioration and corrosion because it is chemically inert under a variety of circumstances. This characteristic is useful in situations that call for a stable substance. Silica also has dielectric qualities and is a good insulator, which makes it helpful in a range of electrical and electronic applications.[131, 132]

1.4.1 Silica in aqueous ionic liquid

Variables like particle size, silica surface modification and ionic liquid composition affect the stability of the silica dispersion in ionic liquid. In order to boost the silica particles' compatibility with the ionic liquid and support dispersion stability, surface modification may be essential. The polarity, viscosity and solvation capacity of various ionic liquids varies. The targeted application and the desired dispersion parameters determine which ionic liquid is best.

The stability and rheology of the colloidal dispersions formed is greatly affected by components like the size, concentration of the particles, hydrophilicity of the ionic liquid and the temperature of the dispersion system. Wittmar *et al.* [133] in their research on the colloidal stability of dispersions of silica nanoparticles in both hydrophilic and hydrophobic imidazolium-based ionic liquid, investigated some of the factors that affect the rheological behaviour of the colloidal dispersions such as concentration and surface rheology of the nanoparticles, hydrophilicity of the ionic liquid and temperature of the system. They reported high compatibility between the hydrophilic ionic liquid and the unmodified hydrophilic nanoparticles, while the hydrophobic ionic liquid also showed increased colloidal stability with silica nanoparticles whose surface was modified with hydrophobic groups. From Figure 1.17, the loss modulus is larger than the storage modulus in the oscillatory tests for the two dispersions of the surface-modified nanoparticles in the hydrophobic ionic liquid, indicating stable dispersions. However, the colloidal dispersion was destabilised when the temperature was raised at higher particle concentration. This shows that the rheological properties of both silica particles and the ionic liquid can be tuned to influence the stability of colloidal dispersions.

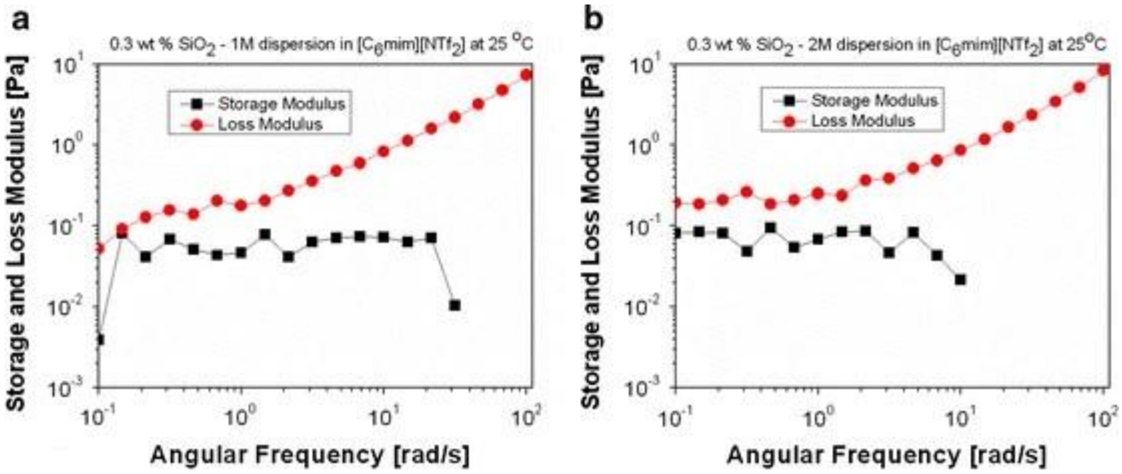


Figure 1.17 [133] Storage and loss modulus versus angular frequency for 0.3 wt % SiO_2 – 1M (left) and SiO_2 – 2M (right) dispersions at 25 °C in hydrophobic ionic liquid. Where 1M and 2M are the two different methods used in the modification of the SiO_2 nanoparticles.

In the research on the impact of lithium salt on fumed silica dispersions' stability in imidazolium-based ionic liquid, Nordstrom *et al.* [134] detailed how silica particles, through the formation of hydrogen bonds, desorbed lithium ions from the surface during gelation of the colloidal dispersions and a little increase in the concentration of the silica particles increased the strength of the gel formed in both the dispersions with lithium salt and without lithium salt.

Ionic liquids have tunable properties that can influence the rheological behaviour of colloidal dispersions of silica.[135, 136] These properties can be adjusted to achieve colloidal stability or otherwise. In the research on colloidal stability of bare and grafted silica nanoparticles with poly(methyl methacrylate) (PMMA), using some imidazolium-based ionic liquids, the bare silica nanoparticles was unstable and formed aggregates in the ionic liquids as a result of screening by surface-charge due to ineffective electrostatic stabilisation in the ionic liquids. However, the PMMA-grafted silica nanoparticles showed prolonged stability in some of the ionic liquids because of efficient steric stabilisation while showing instability in some due to poor solubility.[135] Figure 1.18 shows the stable and the unstable resultant colloidal dispersions.

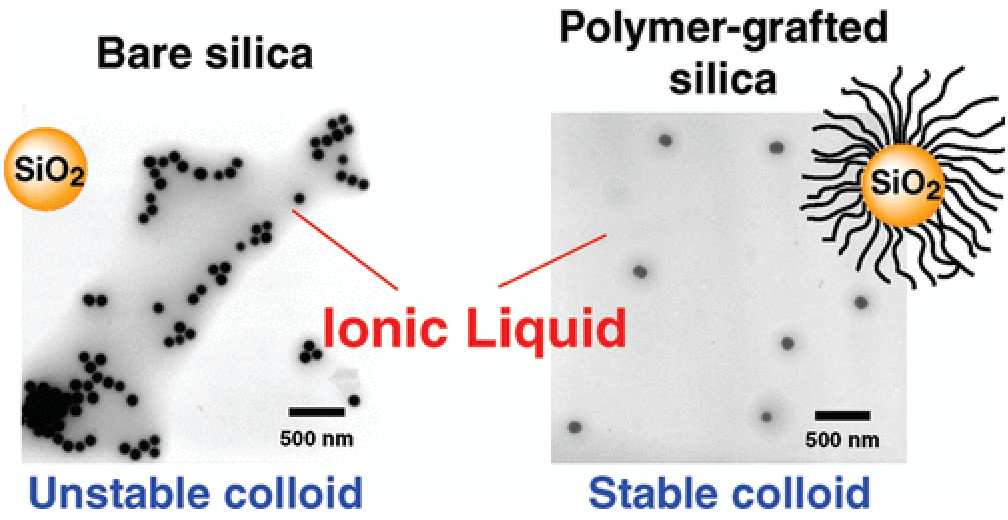


Figure 1.18 [135] Dilute dispersions of silica in ionic liquid showing the formation of stable and unstable colloid.

1.5 Aims and objectives of the research

This study aims to explore the possible applications of ionic liquids as adsorbing surfactants on silica particles in oil-water mixtures for Pickering emulsions. Experiments were carried out using the ionic liquid 1-ethyl-3-methylimidazoliumtetrafluoroborate as the adsorbing surfactant on both Ludox CL and Ludox HS-30 silica nanoparticles and micron-sized silica particles. The objective is to see if the ionic liquid, 1-ethyl-3-methylimidazoliumtetrafluoroborate can serve as an adsorbing surfactant and enhance the stability in Pickering emulsions stabilised by Ludox CL and Ludox HS-30 silica nanoparticles and 2-micron-sized silica particles.

Chapter 2 of this thesis outlines in details, the materials and methods used in carrying out all the experiments in this research. Chapter 3 is the first result chapter and it contains the findings on the silica nanoparticles experiments. This describes two aspects of the silica nanoparticles experiments. First the aqueous dispersion studies of silica nanoparticles in aqueous ionic liquid and the analysis of the resultant stable dispersions of Ludox HS-30 silica nanoparticles using visual inspection and dynamic light scattering for the zeta potential values and particle diameter. Secondly, the report on investigations of silica nanoparticle-stabilised emulsions, prepared by varying the ionic liquid concentration and the use of analytical techniques such as optical microscopy and drop size analysis to investigate and characterise the emulsions formed.

Chapter 4, which is the second result chapter, contains investigations using micron-sized silica particles for both aqueous dispersions and emulsion studies. This chapter contains experiments on using ionic liquid as an adsorbing surfactant on Pickering emulsions stabilised with micron-sized silica particles. It outlines the effects of the method of particle dispersion on the resultant Pickering emulsions' stability.

Investigations were carried out by varying the concentration of both the ionic liquid and the silica particles.

Chapter 5 is an outline of the summary of each chapter and some recommendations for future research.

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Chapter 2 Experimental

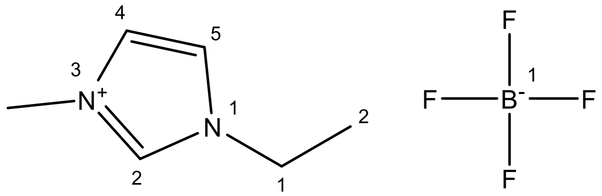
2.0 Background

The different materials and instruments used in this research are outlined in this chapter. In addition, a detailed account of the experimentation methods used are given herein. The methods include the preparation and characterisation of aqueous silica particles, aqueous ionic liquid, aqueous dispersions of silica in IL and octane-in-water emulsions stabilised by silica particles**.**

2.1 Materials

2.1.1 Ionic Liquid (IL)

The ionic liquid, 1-Ethyl 3-methylimidazolium tetrafluoroborate, from Ionic Liquid Technologies, was purchased from Sigma Aldrich. The ionic liquid was received as a clear, viscous light-yellow liquid, ≥ 98 % purity and density 1.287 g/cm^3. Its structure is shown in Figure 2.1.



1-Ethyl 3-methylimidazolium tetrafluoroborate

Figure 2.1 Structure of the IL, 1-ethyl 3-methylimidazolium tetrafluoroborate.

2.1.2 Silica particles

2.1.2.1 Silica nanoparticles

2.1.2.1.1 Ludox® CL colloidal silica

Ludox® CL colloidal silica particles were produced by W.R. Grace & Co. Conn., purchased from Sigma Aldrich and received as a 30 wt.% acidic colloidal suspension in water. The particles are composed of silicon dioxide coated with aluminium oxide ($SiO_2 + Al_2O_3$). They are of density 1.23g/mL at 25 °C, surface area of 230 m^2/g and a particle diameter of 12 nm. They are positively charged and supplied at a pH of 4.5.

2.1.2.1.2 Ludox® HS-30 colloidal silica

This is a 30 wt.% alkaline colloidal silica particle suspension in water, produced by W.R. Grace & Co. Conn. and purchased from Sigma Aldrich. It contains silicon dioxide of density 1.21 g/mL at 25 °C, of surface area 220 m^2/g and has a particle diameter of 12 nm. Ludox HS-30 is negatively charged and was supplied at a pH of 9.8.

2.1.2.2 Silica microparticles

These were received from Fiber Optic Center Inc. as a white powder of particle diameter 2 µm. They were monodispersed.

2.1.3 Oil

The oil used is octane. It was supplied by Sigma Aldrich, ≥ 99% purity and density 0.703 g/cm^3 at 25 °C. It was columned through alumina to further purify it and remove any traces of moisture.

2.1.4 Other materials

The following reagents were received from Fisher Scientific: Ethanol, absolute, ≥ 99.8 % purity; Decon 90, a surface-active detergent for cleaning glassware and microscope slides; sodium hydroxide, > 98.6% purity and hydrochloric acid of purity

37%, both used to adjust the pH of the ionic liquid and silica particles. The water used was deionized water, which was then purified with a Milli-Q reagent system to achieve a resistivity of about 18 MΩ cm.

2.2 Methods

2.2.1 Preparation and characterisation of aqueous IL

Aqueous solutions of the ionic liquid were prepared by measuring the required volume of IL stock solution in water and diluting it with the required volume of Milli-Q water. Aqueous solutions of dilute HCl or NaOH were added to Milli-Q water and utilised to alter the pH of the aqueous ionic liquid as required. The range of concentration of the aqueous IL was from 0 to 1000 mM. A pH meter (Hydrus 300 manufactured by Fisherbrand) was used to measure the pH of the aqueous IL.

2.2.2 Preparation and characterisation of aqueous dispersions of silica particles

Aqueous dispersions of 1 wt.% Ludox CL at low pH of 3.8 ± 0.2 and 1 wt.% Ludox HS-30 at high pH of 9.8 ± 0.2 colloidal silica nanoparticles were prepared by measuring a known volume of the stock particle dispersions and diluting them with the appropriate volume of Milli-Q water. The pH of the aqueous dispersions was measured as described above.

2.2.3 Preparation and characterisation of aqueous dispersions of silica in IL

Equal volumes of known concentration of aqueous dispersions of silica nanoparticles (Ludox CL or Ludox HS-30) and aqueous IL were added together in a glass vial with screw cap and the mixture was hand-shaken for some seconds.

2.2.3.1 Monitoring the stability of the aqueous dispersions of silica in IL

The stability of the aqueous dispersions was monitored by visual inspection and photographs of the vials were taken at time intervals of 0, 24-48 h, 1 week, 2 weeks and 3 weeks.

2.2.3.2 Measurement of zeta potential and particle size

The zeta potential of silica nanoparticles was measured at 25 ^{o}C with a Zetasizer Nanoseries Nano-ZS Malvern Instruments. 1 ml of aqueous silica nanoparticle dispersion in aqueous IL was measured for each IL concentration into a 4.5 ml polystyrene disposable cuvette and placed in the instrument. This procedure was repeated three times for each IL concentration of the aqueous dispersion. After each run, the dip cell was first rinsed with ethanol, then Milli-Q water and dried using compressed air before the next run. The same procedure was repeated for particle size measurement but without introducing the dip cell. Ludox CL dispersions at high IL concentrations were sonicated for 6 min using an ultrasonic bath (Ultrawave) before measurement to ensure no sedimentation.

Figure 2.2 Zetasizer Nanoseries (Nano-ZS Malvern Instruments)

2.2.4 Preparation and characterisation of emulsions stabilised by silica nanoparticles

The required concentration and volume of aqueous dispersion of silica nanoparticles and the required concentration and volume of aqueous IL (5ml aqueous phase) were added to a 20 ml screw cap glass vial with dimensions 51 mm by 27 mm and the contents hand-shaken for a few sec. Then, an equal volume of octane (5 ml) was added, and the two phases were homogenised using an Ultra-Turrax T-25 homogenizer between

12,000 and 13,000 rpm for 2 min. An immediate photo' of the emulsion was taken and the whole process repeated for all the IL concentrations. Every experiment was conducted at room temperature of about 20 ^{o}C.

Figure 2.2 Photo of Ultra-Turrax T-25 homogenizer.

2.2.5 Measurement of three-phase contact angle

The three-phase contact angle at the octane-water interface was measured using a Drop Shape Analysis System DSA 10 Mk2. First, microscope glass slides (Fisher Scientific) were cleaned with Decon-90 in order to mimic anionic silica particles. The slide was put into a rectangular glass cuvette and octane was gently added to submerge the slide. Then, a drop of aqueous IL of known concentration was placed onto the slide using a 25 μL microvolume syringe. Different concentrations of aqueous IL were prepared using aqueous NaOH to raise the pH of the aqueous IL to about 10. Then, the contact angle of the different IL concentrations at the octane-water-glass interface was measured. Three to five measurements were done for each IL concentration and the whole procedure was repeated for all IL concentrations.

Figure 2.3 Drop Shape Analyser (DSA 10 Mk2).

2.2.6 Preparation and characterisations of emulsions stabilised by silica microparticles

Emulsions stabilised by silica microparticles were prepared using three different methods which are: particles originally dispersed in water, particles originally dispersed in octane and the powdered particle method described below. The concentration of silica microparticles used was from 0 to 4 wt.%.

2.2.6.1 Silica particles originally dispersed in water

The required mass of microparticles was put in a vial with screw cap containing the required volume of Milli-Q water. Aqueous NaOH was used to raise the pH to about 10. Thereafter, the vial was covered and put in an ultrasonic bath to sonicate and disperse the particles in water for about 8 min.

Then, the required volume and concentration of aqueous IL (at pH 10) was added, hand shaken for a few seconds and an equal volume of octane added. The two phases were homogenised at 12,000 to 13,000 rpm for 2 minutes using an Ultra-Turrax T-25 homogenizer.

2.2.6.2 Silica particles originally dispersed in oil

The required mass of silica particles was put into a glass vial with screwcap containing 5 ml of octane. The vial was placed in a Branson Digital Sonifier with low power ultrasonic finger and cooled in a beaker of ice to disperse the particles in oil. An amplitude of 40% for 30 sec at 0.5 pulse on and 0.5 pulse off was used.

After dispersing the particles in oil, 5 ml of the required aqueous IL concentration at pH 10 was added and the two phases were homogenised for 2 min at 12,000 to 13,000 rpm using an Ultra-Turrax T-25 homogenizer. An immediate photo’ was taken and the whole process repeated for all aqueous IL concentrations.

2.2.6.3 Powered silica particle method

The powdered silica particle method was done by placing a mass of powdered silica in a glass vial with screwcap and simultaneously adding equal volumes of both the aqueous phase (containing the required IL concentration at pH 10) and octane. The mixture was homogenised for 2 min at 12,000 to 13,000 rpm using an Ultra-Turrax T-25 homogenizer. An immediate photo’ was taken and the whole process repeated for all aqueous IL concentrations.

2.2.6.4 Determination of emulsion type

The drop test was conducted on all emulsions to determine the emulsion type. A volumetric pipette was used to take a small sample of the emulsion, which was separately added into octane and water. If the emulsion dispersed in octane, then it is water-in-oil (w/o). If it dispersed in water, then it is oil-in-water (o/w).

2.2.6.5 Emulsion stability monitoring

The stability of the prepared emulsions was monitored by visual inspection for possible coalescence or creaming and photos of the vials were taken using a digital camera at time intervals of 0, 24-48 h, 1 week, 2 weeks and 3 weeks. An o/w emulsion's stability to creaming was evaluated by tracking the position of the water-emulsion interface, whereas the stability to coalescence was evaluated by monitoring the position of the oil-emulsion interface. The emulsion stability was determined from a plot of average drop diameter against either [IL] or [particle] and from the values of f_o and f_w, where f_o relates to the stability to coalescence and f_w relates to the stability to creaming:

$$f_o = \frac{volume\ of\ oil\ released}{initial\ volume\ of\ oil} \tag{2.1}$$

$$f_w = \frac{volume\ of\ water\ released}{initial\ volume\ of\ water} \tag{2.2}$$

The extreme values of f_o and f_w are maximum value = 1 and minimum value = 0. Hence, when f_o or $f_w = 1$, there is complete stability to coalescence or creaming respectively and when fo or fw = 0, there is complete instability and complete phase separation occurs.

2.2.6.6 Optical microscopy

Optical microscopy was performed using an Olympus BX51 microscope to capture the images of the stable emulsions 3 to 4 weeks after homogenisation. A drop of the diluted emulsion was put on a microscope slide after the emulsions had first been diluted using the continuous phase and the image observed at different magnifications. The droplet shape and average diameter were determined afterwards.

Figure 2.4 Olympus BX51 microscope.

Chapter 3

3.0 Aqueous dispersions and emulsions stabilised by silica nanoparticles

Background:

Ionic liquids as adsorbing surfactants can be used to enhance the stability of emulsions stabilised by silica nanoparticles. This chapter contains a comprehensive experimental account of the aqueous dispersions of silica nanoparticles in 1-ethyl-3-methylimidazolium tetrafluoroborate (IL), and emulsions stabilised by silica nanoparticles, with the IL as the adsorbing surfactant. The dispersions of silica nanoparticles in aqueous ionic liquid (IL) were first studied and characterised using dynamic light scattering for zeta potential and particle size measurements. Emulsions stabilised by silica nanoparticles were also studied and characterised using optical microscopy (Olympus microscope). All experiments were carried out at room temperature of 20 ± 1 ^{o}C.

3.1 Aqueous dispersions of silica nanoparticles in aqueous ionic liquid

Aqueous dispersions of Ludox CL and Ludox HS-30 silica nanoparticles in aqueous IL were studied and characterised. The concentrations quoted are relative to the aqueous dispersion for both silica nanoparticles and ionic liquid.

3.1.1 Ludox CL dispersions at low pH

Figure 3.1 shows the of appearance of 1 wt.% Ludox CL dispersions in increasing IL concentrations (1:1 volume of Ludox CL:IL) between 0 and 0.1 M at pH = 3.6 ± 0.1 immediate photo, 72 hours and 3 weeks after preparation. The dispersions were stable at low IL concentrations. As the concentration of IL increases, the dispersions becomes slightly turbid, with sedimentation occurring at high IL concentrations. This affirms the instability of the formed aqueous dispersions in the IL, in line with the sedimentation method used to evaluate the stability of nanofluids [1,2,3].

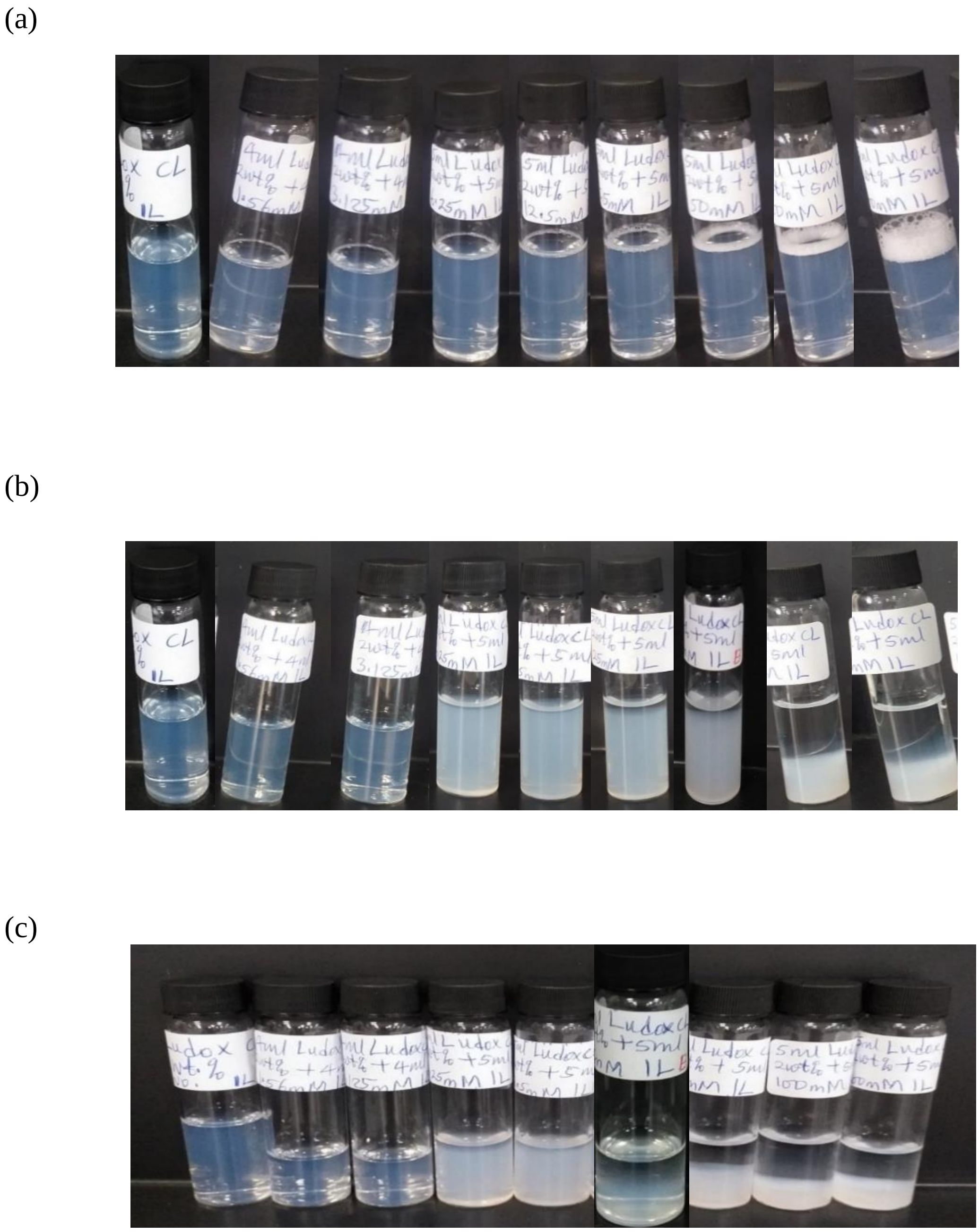


Figure 3.1. Appearance of 1 wt.% Ludox CL dispersions at pH = 3.6 in aqueous IL for [IL]/M from left to right of: 0, 0.00078, 0.0016, 0.0031, 0.0063, 0.013, 0.025, 0.050 and 0.10 (a) immediately after preparation, (b) after 72 h, (c) after 3 weeks.

The zeta potential of the aqueous dispersions in IL was measured as an indication of the potential stability of the aqueous dispersions. Figure 3.2 shows a plot of zeta potential of the dispersions as a function of IL concentration. In the absence of IL, the zeta potential value was +34 mV. As the IL concentration gradually increased, the zeta potential value changed from above +30 mV to lower negative values and finally to lower positive values as the IL concentration increases. The drop in the value of the zeta potential with increasing IL concentration indicates decreasing stability [4,5,6,7].

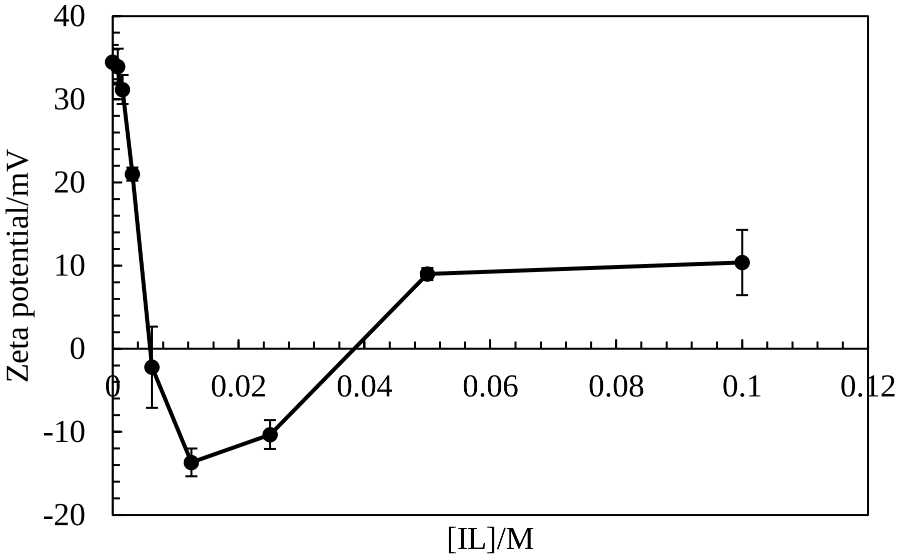


Figure 3.2. Zeta potential of 1 wt.% Ludox CL dispersions *versus* [IL] at pH 3.6.

Figure 3.3 is a plot of the average particle diameter as a function of IL concentration for 1 wt.% Ludox CL dispersions. As the concentration of IL increases, the apparent particle size also increases. This can be attributed to aggregation of the particles.

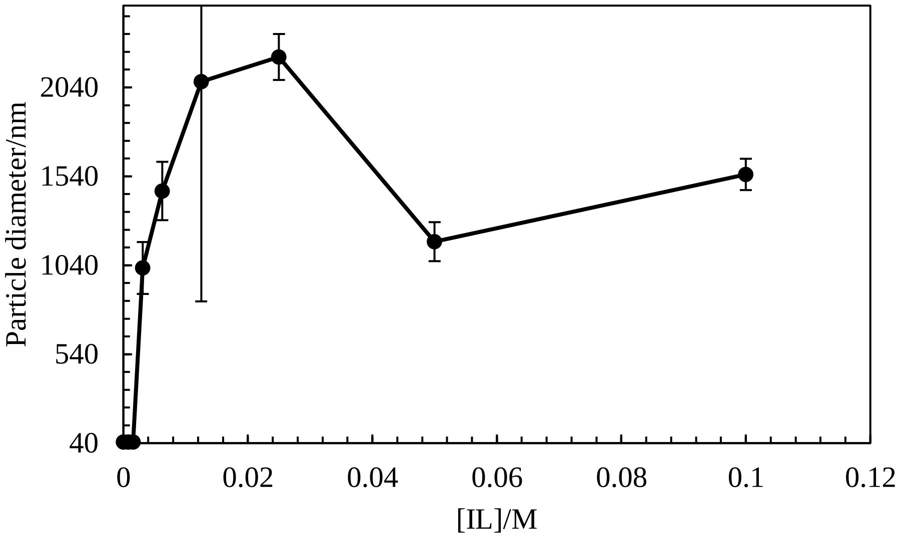


Figure 3.3. Plot of particle size of 1 wt.% Ludox CL dispersions *versus* [IL] at pH 3.6.

3.1.2 Ludox HS-30 dispersions at high pH

Figure 3.4 shows the appearance of 1 wt.% Ludox HS-30 dispersions in increasing IL concentrations between 0 and 0.05 M immediately after preparation, 72 hours and 3 weeks after at pH 10. The dispersions appeared to be stable, less turbid at low IL concentrations, and more turbid as the IL concentration increases. This suggests dispersion instability within the IL concentrations studied. However, unlike Ludox CL dispersions, no obvious sedimentation was observed with time at higher IL concentrations. This agrees with the work of Ueno *et al*. in a study of bare and poly(methyl methacrylate) (PMMA)-grafted silica nanoparticles in 1-alkyl-3-methylimidazolium-based ionic liquids of different structures, where the bare silica particles were unstable while the PMMA-grafted silica particles displayed long-term colloidal stability[8].

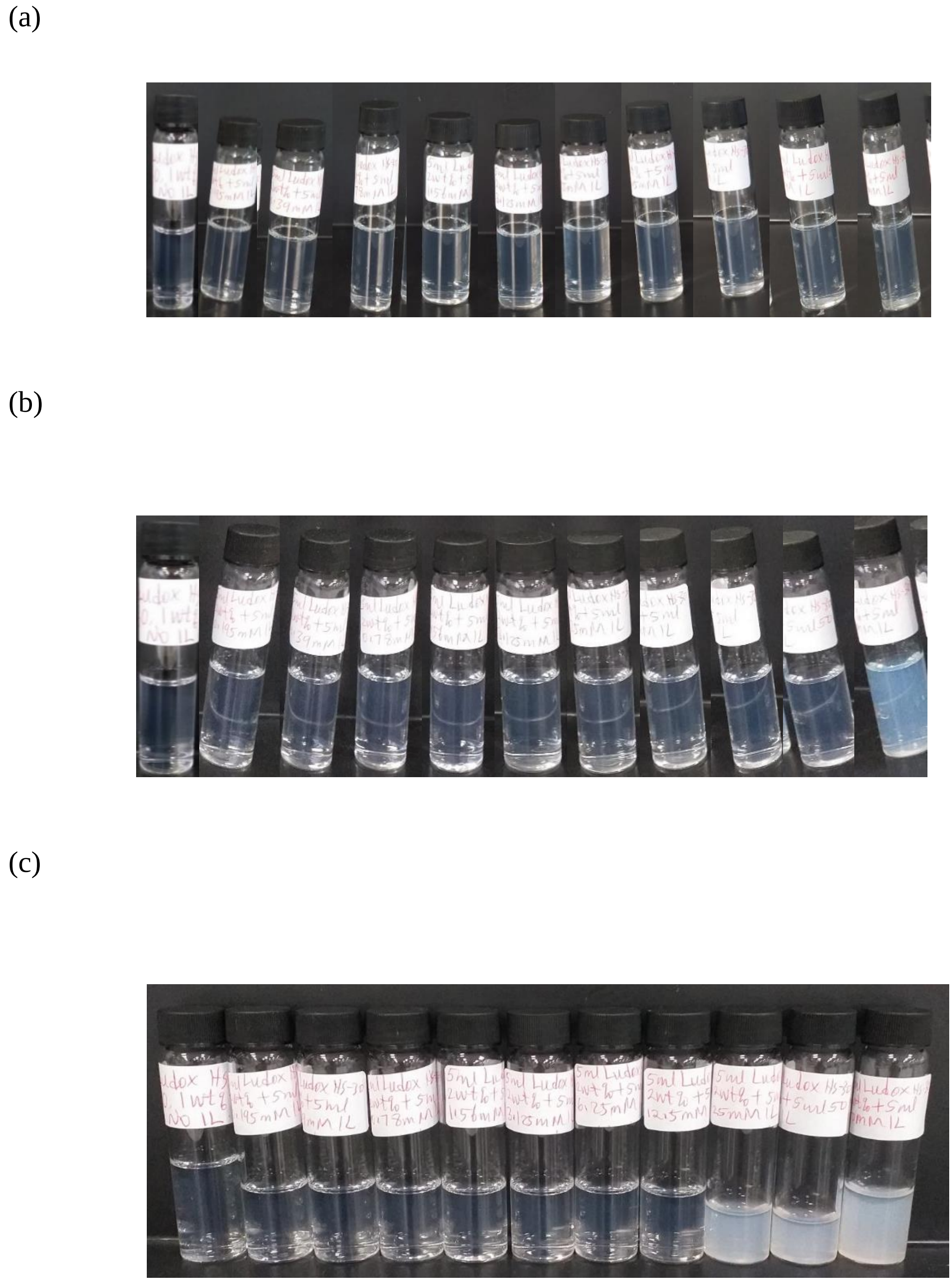


Figure 3.4. Appearance of 1 wt.% Ludox HS-30 dispersions at pH 10 in aqueous [IL]/M from left to right of: 0, 0.000098, 0.000195, 0.00039, 0.00078, 0.0016, 0.0031, 0.0063, 0.013, 0.025 and 0.050 (a) immediately after preparation, (b) 72 hours and (c) 3 weeks after.

Figure 3.5 shows a plot of the zeta potential of 1 wt.% Ludox HS-30 dispersions as a function of IL concentration. As the concentration of IL increases from 0 to 0.0063 M, the zeta potential was high negative values of approximately -30 mV, and these dispersions were less turbid and seem to be the most stable in the range of the IL concentrations studied. However, as the IL concentration increases beyond this, the zeta potential reduces to lower negative values up to -20 mV. The dispersions formed at these higher IL concentrations appear more turbid, suggesting reduced stability with time. The reduction in value of the zeta potential as the IL concentration increases can be attributed to factors such as the isoelectric point and adsorption of IL on particles,[9,10] and steric effects [11]. The zeta potential can be used to evaluate the stability of dispersions. It was observed that as the IL concentration increases, the stability of the dispersions reduced due to the decrease in the values of the zeta potential. Based on the foregoing, further increase in the IL concentration and fall in the zeta potential values could result to aggregation and possible sedimentation of the particles [12].

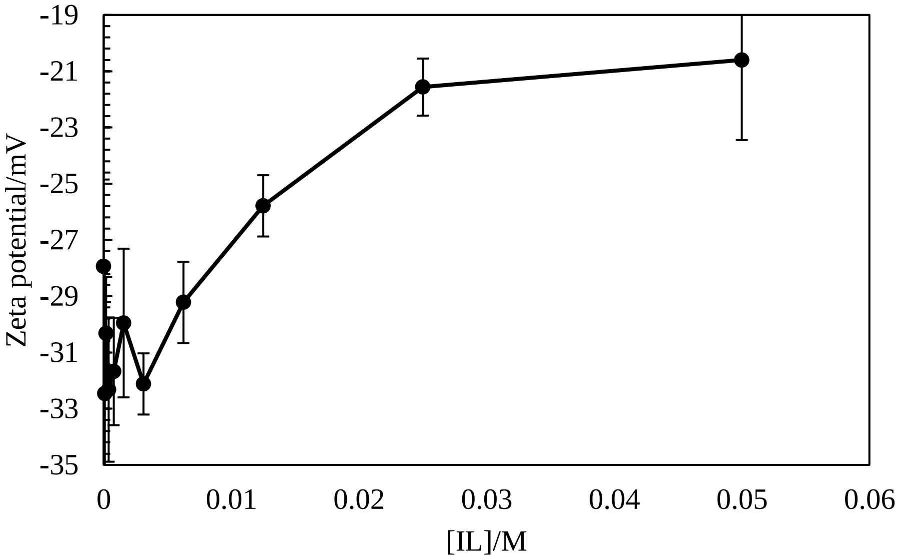


Figure 3.5. Zeta potential of 1 wt.% Ludox HS-30 dispersions *versus* [IL] at pH 10.

Figure 3.6 is a plot of the average particle diameter as a function of IL concentration for 1 wt.% Ludox HS-30 dispersions. A similar trend to what was seen with Ludox CL dispersions was also observed, where dispersions at higher IL concentrations recorded the highest particle size values. This suggests aggregation of particles[12], hence increased dispersion instability as IL concentration increases.

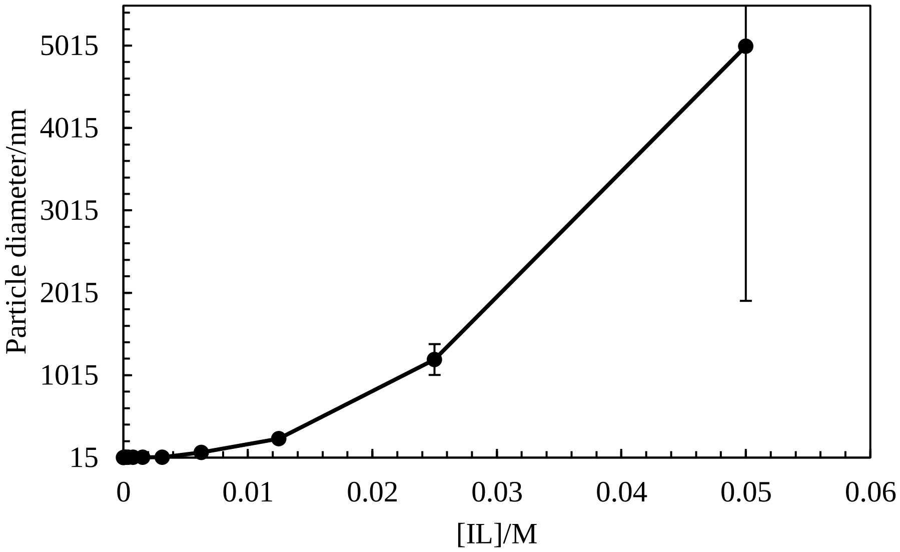


Figure 3.6. Particle diameter of 1 wt.% Ludox HS-30 dispersions *versus* [IL] at pH 10.

3.2 Ionic liquid as surfactant in Pickering emulsions stabilised by silica nanoparticles

The silica nanoparticle dispersions study was followed by experiments on emulsions stabilised by both Ludox CL and Ludox HS-30 and the IL acted as the surfactant. The emulsions were characterised by optical microscopy and drop shape analyser (contact angle). Control experiments on emulsions containing either silica nanoparticles alone or aqueous IL alone were first prepared and investigated. Afterwards, equal volumes of the aqueous and oil phases (1:1 volume) stabilized by silica nanoparticles were homogenised and investigated.

3.2.1 Effect of IL concentration at constant Ludox CL concentration at pH 3.6

The concentration of Ludox CL was kept constant at 2 wt.% while the IL concentration was varied from 0 to 1000 mM. Figure 3.7 shows the appearance of the control experiments on emulsions of (a) 2 wt.% Ludox CL without IL and (b) a range of IL concentrations without Ludox CL particles. It can be observed that there was no formation of stable emulsions immediately after homogenisation in both cases. Rather, complete phase separation was observed a few minutes after preparation. This shows that both Ludox CL particles or aqueous IL when used alone cannot successfully stabilise emulsions.

(a)

(b)

Figure 3.7 Appearance of emulsions of 2 wt.% Ludox CL and octane (1:1 volume) for (a) without IL immediately (left) and a few mintes later (right) and (b) without Ludox CL immediately (upper) and a few minutes later (lower) for [IL]/mM from left to right: 0, 0.39, 0.78, 1.56, 3.125, 6.25, 12.5, 25, 50, 100, and 200.

Figure 3.8 shows the appearance of emulsions stabilized by 2 wt.% Ludox CL and increasing concentrations of aqueous IL at pH 3.6 monitored over a period of 0, 24 hour and up to 4 weeks. Complete phase separation occurred a few minutes after homogenisation, with increasing particle sedimentation as the concentration of IL increases. This shows that the anion of the IL either does not adsorb on positively charged particles or to a sufficient extent to modify their wettability.

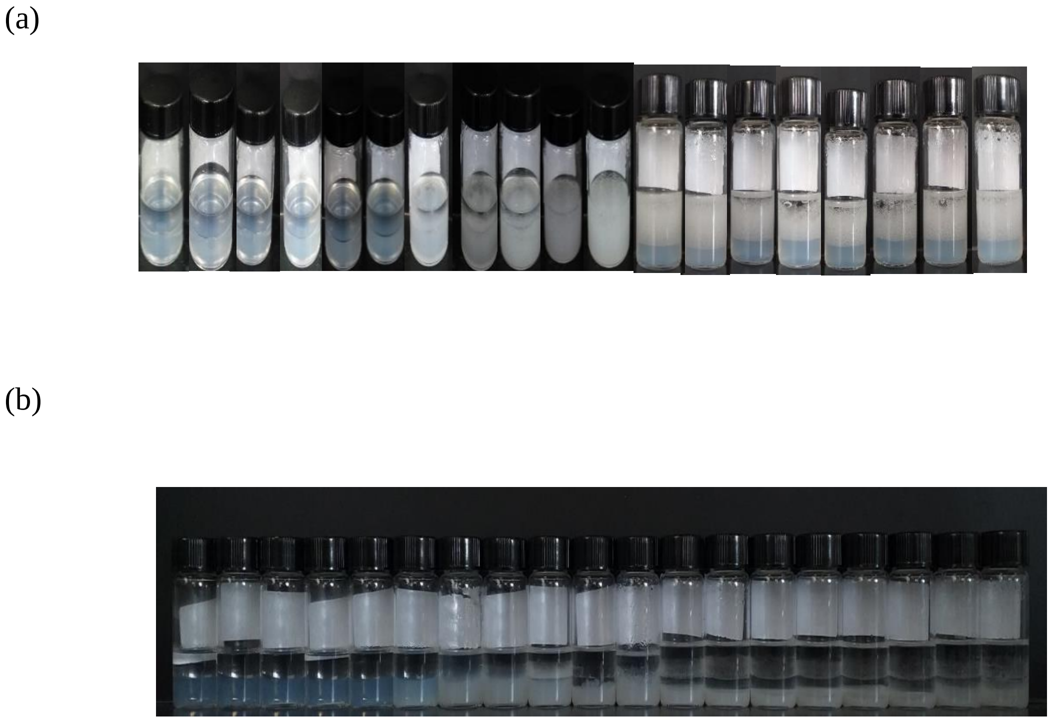


Figure 3.8 Appearance of emulsions of 2 wt.% Ludox CL with aqueous IL and octane (1:1 volume) for [IL]/mM from left to right: 0, 0.39, 0.78, 1.56, 3.125, 6.25, 12.5, 25, 50, 100, 200, 300, 400, 500, 600, 700, 800, 900 and 1000 at pH 3.6 (a) immediately and (b) 4 weeks after.

3.2.2 Effect of IL concentration at constant Ludox HS-30 concentration at pH 10

At constant Ludox HS-30 concentration of 2 wt.%, the IL concentration was varied from 0 to 900 mM. Figure 3.9 is the control experiment on emulsions stabilised by 2 wt.% Ludox HS-30, (a) without IL, and (b) without the particles. It shows the formation of unstable emulsions which completely phase separated a few minutes after preparation. Thus both Ludox HS-30 and aqueous IL when used alone cannot stabilise octane-water emulsions.

(a)

Figure 3.9. (a) Appearance of emulsions of 2 wt.% Ludox HS-30 and octane (1:1 volume) without IL. Immediate photo (left) and a few minutes after photo (right).

(b)

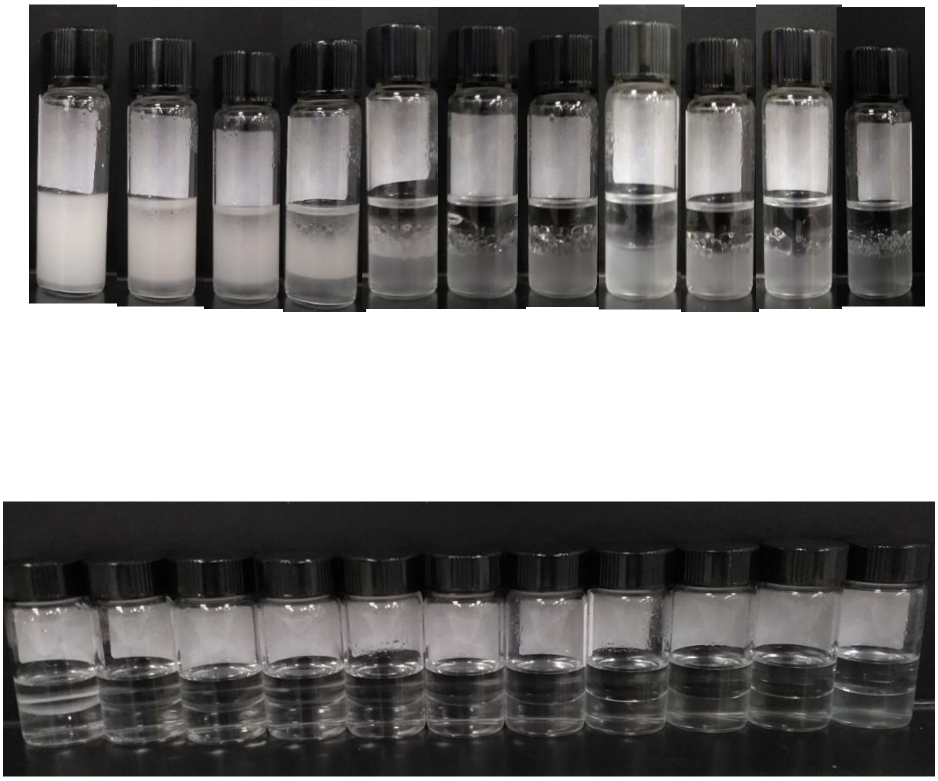


Figure 3.9. (b). Appearance of emulsions of equal volumes of IL and octane, immediate photo and a few minutes later photo, for [IL]/mM from left to right: 0, 0.39, 0.78, 1.56, 3.125, 6.25, 12.5, 25, 50, 100, and 200.

Figure 3.10 shows the appearance of emulsions stabilized by 2 wt.% Ludox HS-30 and increasing concentrations of aqueous IL at pH 10 observed over a timeframe of 0, 24 hours and up to 4 weeks. The results show that no stable emulsions were formed at low IL concentrations from 0 to 12.5mM, stable oil-in-water (o/w) emulsions formed at intermediate IL concentrations from 50mM to 200mM while no stable emulsions formed at IL concentrations above 200mM. The formation of stable emulsions by Ludox HS-30 confirms that the surface of the Ludox HS-30 nanoparticles produced enough repulsion to sufficiently counterbalance attractive forces by the IL, thereby stabilizing the emulsions [13]. This implies that 1-ethyl-3-methylimidazolium ion, which is the cation of the IL, can modify the negatively charged Ludox HS-30 particle surfaces at intermediate IL concentrations, enabling emulsification. This finding is in line with the result obtained by Shi *et al.*, where negatively charged silica nanoparticles were used with CO_2-responsive ionic liquids to prepare reversible stable Pickering emulsions [14]. This also agrees with the work of Binks *et al*, which formed stable o/w Pickering emulsions using Pb-supported silica nanoparticles with azobenzene ionic liquid as the adsorbing surfactant [15] and effective preparation of a series of novel stable emulsions containing ionic liquid exclusively stabilised by silica nanoparticles, although they used IL and oil to vary the inherent particle hydrophobicity [16].

(a)

(b)

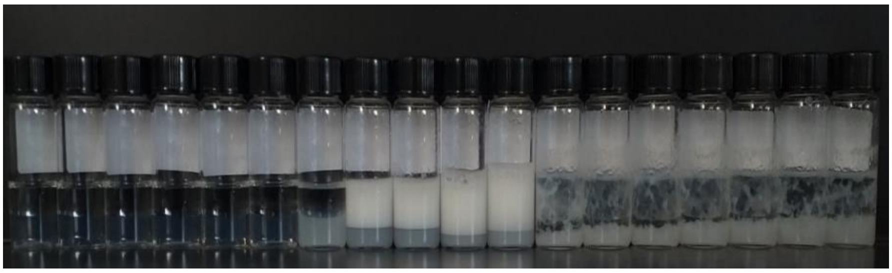
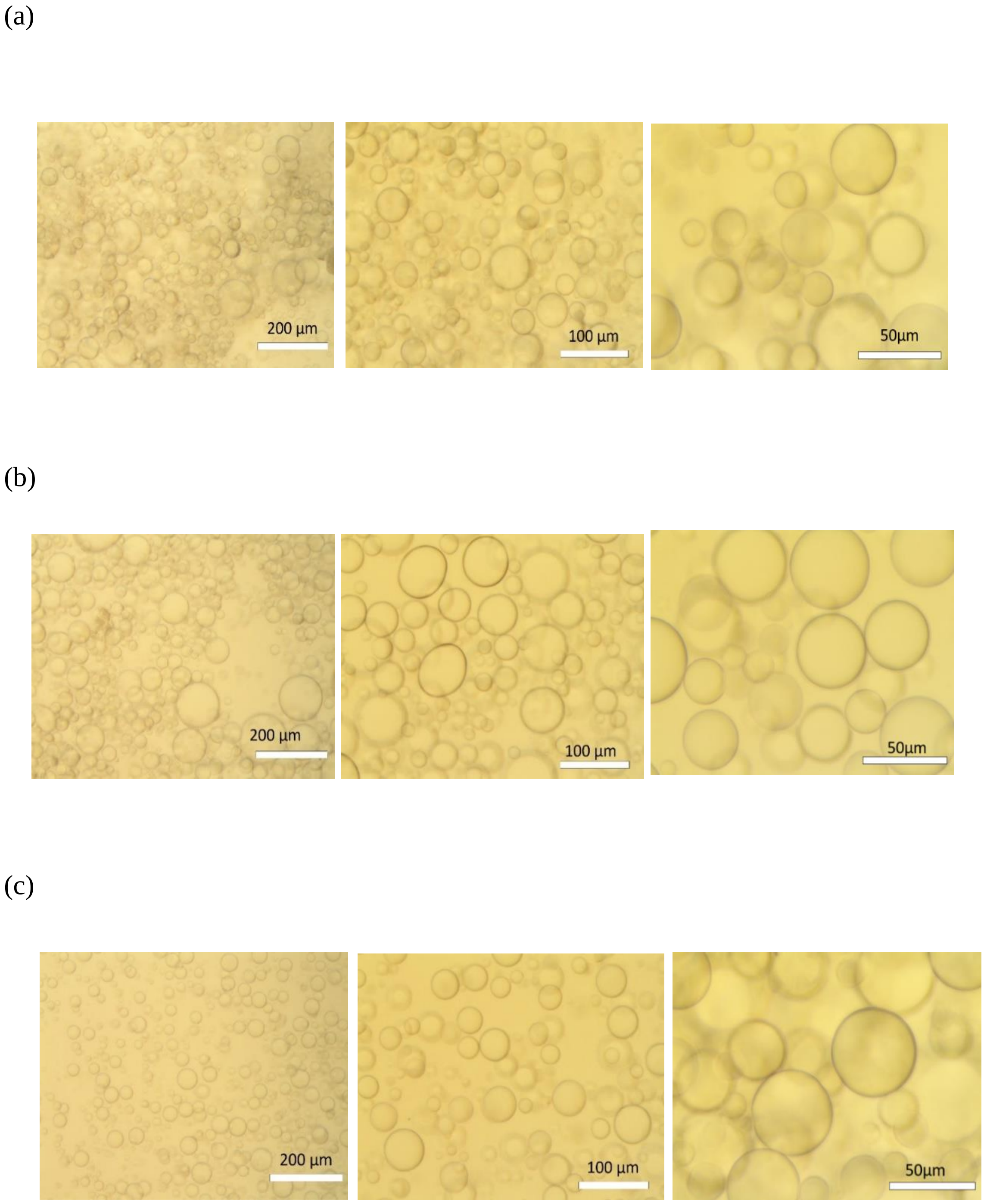


Figure 3.10. Appearance of emulsions containing 2 wt.% Ludox HS-30 for [IL]/mM from left to right: 0, 0.39, 0.78, 1.56, 3.125, 6.25, 12.5, 25, 50, 100, 200, 300, 400, 500, 600, 700, 800 and 900 at pH = 10 (a) immediately after preparation and (b) 4 weeks after.

Optical microscopy analysis was done on the stable o/w emulsions to determine the shape and the average diameter of the droplets formed. Figure 3.11 shows the optical images formed at intermediate IL concentrations 4 weeks after preparation. Spherical droplets were observed on all the images. The average droplet diameter increased from 16 µm to 24 µm, and further reduced to 16 µm at ± 0.4 µm as the IL concentration increased.


(a)
200 µm
100 µm
50µm
(b)
200 µm
100 µm
50µm
(c)
200 µm
100 µm
50µm

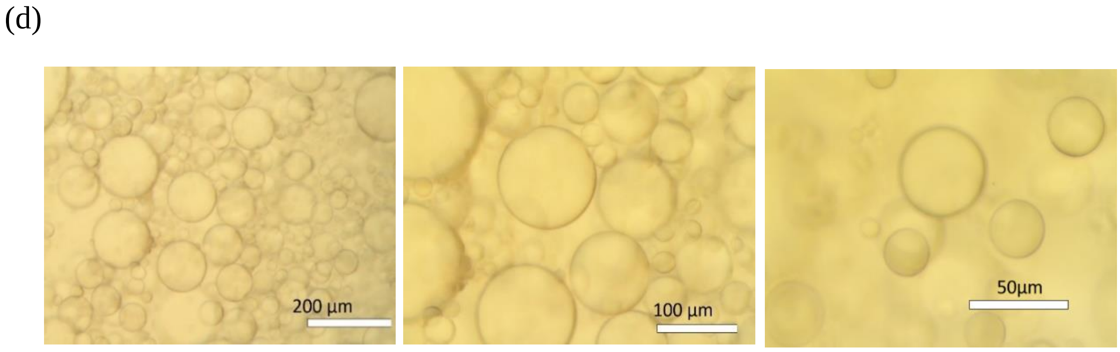


Figure 3.11. Optical microscopy images of 2 wt.% Ludox HS-30 emulsions after 4 weeks for IL concentrations of (a) 25 mM, (b) 50 mM, (c) 100 mM and (d) 200 mM at different magnifications.

A measure of the stability to coalescence (f_o) and the stability to creaming (f_w) was done to ascertain the stability of the o/w emulsions to both coalescence and creaming. Figure 3.12 is a plot of f_o and f_w as a function of IL concentration for the stable emulsions 4 weeks after preparation. From figure 3.12, the f_o curve is a minimum, showing maximum coalescence of 1 at zero IL concentration, zero coalescence at IL concentrations of 0.025M, 0.05M, 0.1M and 0.2M, and rapid increase in coalescence to 1 at higher IL concentrations from 0.4M to 0.9M. This indicates that the o/w emulsions formed at IL concentrations from 0.025M to 0.2M were very stable to coalescence. The f_w curve is also a minimum with highest creaming value of 1 at zero IL concentration, reduced but not zero creaming observed at IL concentrations from 0.025M to 0.2M and sharp increase in creaming to a maximum of 1 at higher IL concentrations from 0.4M to 0.9M. This shows that the o/w emulsions formed were more stable to coalescence than to creaming at IL concentrations of 0.025M, 0.05M, 0.1M and 0.2M, affirming what is expected in o/w emulsions. These observations could be linked with the findings in the studies of the aqueous dispersions of Ludox HS-30, where the aqueous dispersions in IL appeared stable with no sedimentation of particles at similar IL concentrations of 0.013M, 0.025M and 0.050 M but with half the particle concentration. The sedimentation of the o/w emulsion particles at higher IL concentrations from 0.3 M to 0.9 M also aligns with the expected possibility of sedimentation and increasing instability of the aqueous dispersions of Ludox HS-30 at higher IL concentrations. This confirms increasing instability with increasing IL concentration for both the aqueous dispersions and the emulsions of Ludox HS-30.

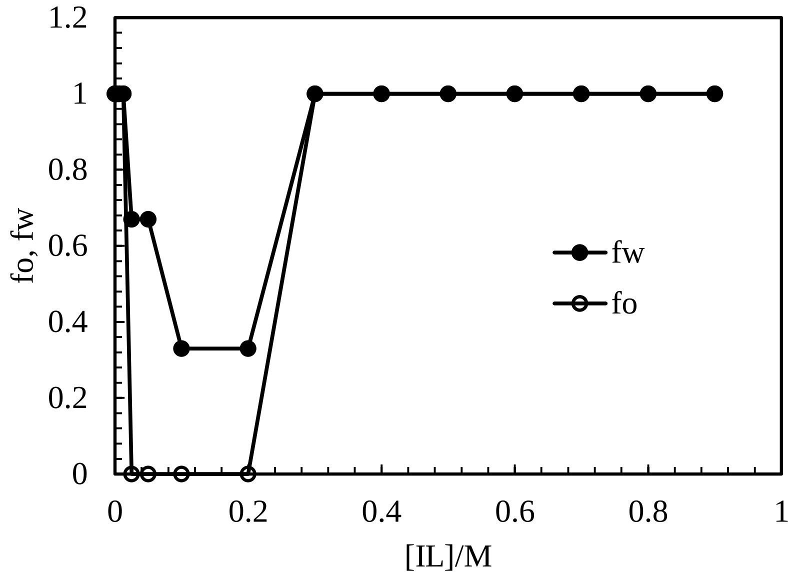


Figure 3.12. Plot of f_o (stability to coalescence) and f_w (stability to creaming) as a function of IL concentration for o/w emulsions of 2 wt.% Ludox HS-30 and 4 weeks after preparation.

The contact angle was measured in order to determine the hydrophilicity and surface properties of the silica nanoparticles and its wettability by the IL [17]. Hence the microscopic glass slides were modified to mimic a hydrophilic silica surface of Ludox HS-30 nanoparticles. Figure 3.13 shows a plot of the average contact angle of a water drop (pH 10) under octane on hydrophilic glass slides at different IL concentrations. The average contact angle for Milli-Q water was less than 5°. The contact angle increased from less than 5° to 38° at 0.00078 M IL. As the concentration of IL increased, the contact angle value gradually dropped to 17° at 0.1 M and later increased to 33° at [IL] of 0.9 M, at ± 0.4°. All the contact angle values are much less than 90° affirming the high hydrophilicity of the silica nanoparticles and the resultant high wettability of the Ludox HS-30 particles in water, hence the resultant formation and stability of oil-in-water emulsions [18,19].

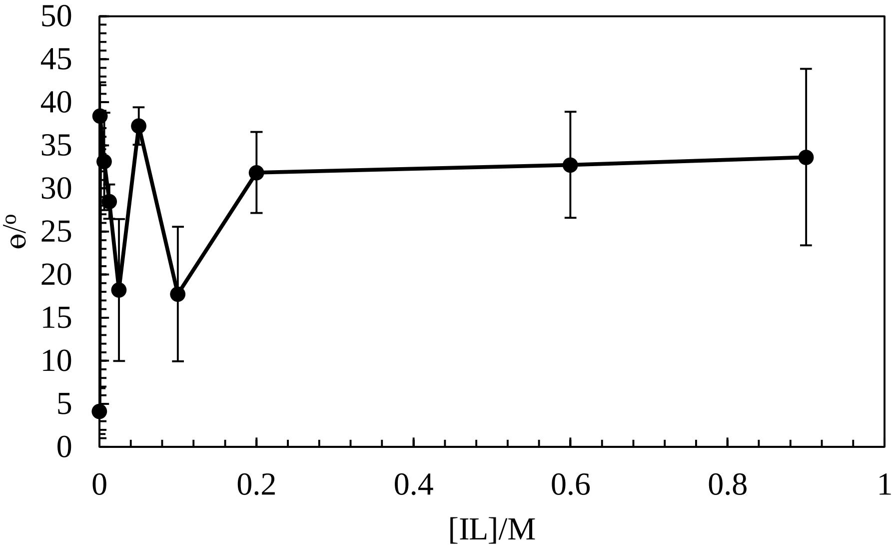


Figure 3.13. Plot of contact angle of a water drop (pH 10) on a hydrophilic glass slide under octane as a function of IL concentration. Contact angle of Milli-Q water is < 5°.

3.3 Conclusions:

This chapter researched on aqueous dispersions of silica nanoparticles in 1-ethyl-3-methylimidazolium tetrafluoroborate (IL) as well as emulsions stabilised by silica nanoparticles, with the IL serving as the adsorbing surfactant.

The effect of IL concentration on the stability of both the aqueous dispersions and the emulsions was investigated. Ludox HS-30 silica nanoparticles formed more stable aqueous dispersions with no sedimentation observed at the studied IL concentrations than

Ludox CL, which formed less stable aqueous dispersions with sedimentation observed at higher IL concentrations.

The effect of the zeta potential value on the stability of the dispersions was looked at. The zeta potential values for Ludox CL changed from +34 mV to lower negative values and finally to lower positive values as the IL concentration increases, suggesting reduced dispersion stability with increasing IL concentration. For the Ludox HS-30, the zeta potential value changed from higher negative (-30 mV) to lower negative value as the IL concentration increases, suggesting reduced stability at higher IL concentrations. The particle size also increased as the IL concentration increases, suggesting aggregation of particles and reduced stability for both Ludox CL and Ludox HS-30 silica nanoparticles.

The findings of the emulsion studies aligns with that of the aqueous dispersions, with Ludox HS-30 forming stable o/w emulsions at intermediate IL concentrations while Ludox CL formed no stable emulsions at the IL concentrations studied. Hence the IL was able to act as an adsorbing surfactant by enhancing the stability of the o/w emulsions stabilised by Ludox HS-30 silica nanoparticles at intermediate IL concentrations. This shows that the cation of the IL can modify the anion of Ludox HS-30 to form stable o/w emulsions while the anion of the IL cannot modify the cation of the Ludox CL, hence no stable emulsions formed. Also, increasing the IL concentrations reduces the stability for both the aqueous dispersions and the emulsions studies.

3.4 REFERENCES

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Chapter 4

4.0 Micron-sized silica particles

Background:

Ionic liquids can serve as adsorbing surfactants to increase the stability of emulsions stabilised by micron-sized silica particles. This chapter researched on the ionic liquid, 1-ethyl-3-methylimidazolium tetrafluoroborate, as an adsorbing surfactant in Pickering emulsions stabilised by micron-sized silica particles using three different methods to disperse the silica particles before homogenisation. Following the findings of emulsions stabilised by silica nanoparticles, studies on emulsions stabilised by micron-sized silica particles of about 2 µm were carried out and the findings detailed in this chapter. This was to ascertain if ionic liquid as an adsorbing surfactant also applies to Pickering emulsions stabilised by larger particles and to visualise the particles on emulsion droplet interfaces using optical microscopy. Prior to commencing the emulsion studies, aqueous dispersions of micron-sized silica particles in ionic liquid were investigated. All experiments were done at room temperature of 20 ± 1 ^{o}C and at pH ~ 10.

4.1 Aqueous dispersions of micron-sized silica particles in ionic liquid

Figure 4.1 shows the appearance of aqueous dispersions of 2 wt. % silica particles of diameter 2 µm in ionic liquid for IL concentrations between 0 and 4.5×10^{-1} M at pH ~ 10. The dispersions were cloudy and turbid immediately after preparation for all IL concentrations studied. However, this was followed by an increasing rate of sedimentation with increasing IL concentration a few minutes after preparation. After 24 hours, complete sedimentation was observed with an upper clear layer and a lower particle sediment for all IL concentrations.

(a)

(b)

Figure 4.1. Appearance of 2 wt.% micron-sized silica particle (diameter 2 μm) dispersions in aqueous IL for [IL]/M from left to right of: 0, 3.9×10^{-4}, 1.56×10^{-3}, 3.13×10^{-3}, 6.25×10^{-3}, 1.25×10^{-2}, 2.5×10^{-2}, 5.0×10^{-2}, 1.0×10^{-1}, 1.5×10^{-1}, 2.0×10^{-1}, 2.5×10^{-1}, 3.0×10^{-1}, 3.5×10^{-1}, 4.0×10^{-1}, and 4.5×10^{-1} at pH ~ 10 for (a) immediately after preparation and (b) 24 hours later.

4.2 Pickering emulsions stabilised by micron-sized silica particles

Experiments with micron-sized silica particles were carried out using three different approaches depending on how the silica particles were introduced into the system: (i) Particles originally dispersed in water, (ii) particles originally dispersed in octane and (iii) powdered particle method, where water and octane were simultaneously added to particles. All the experiments contained a fixed particle concentration of 2 wt. %

with respect to the aqueous phase, at pH ~ 10 and at room temperature of 20 ± 1 °C. The type of emulsion formed was oil-in-water (o/w) using the drop test [1, 2].

4.2.1 Particles originally dispersed in water

An optical micrograph of 2 μm silica particles dispersed in water is shown in Figure 4.2. It is seen that particles dispersed discretely in water.

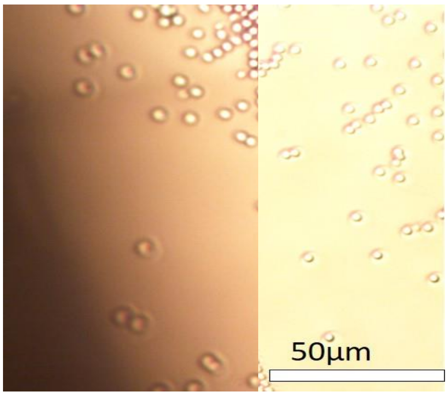


Figure 4.2. Microscope image of 2 wt. % micron-sized silica particles dispersed in water at pH ≈10.

The appearance of o/w emulsions with particles originally dispersed in water for IL concentrations from 0 to 4.0×10^{-1} M at different times since preparation is shown in Figure 4.3. Partial phase separation can be seen at IL concentrations between 0 and 2.5×10^{-2} M. A stable emulsion to coalescence forms at an intermediate IL concentration of 5.0×10^{-2} M, after which there was increasing phase separation and eventual complete phase separation at IL concentrations > 1.0×10^{-1} M.

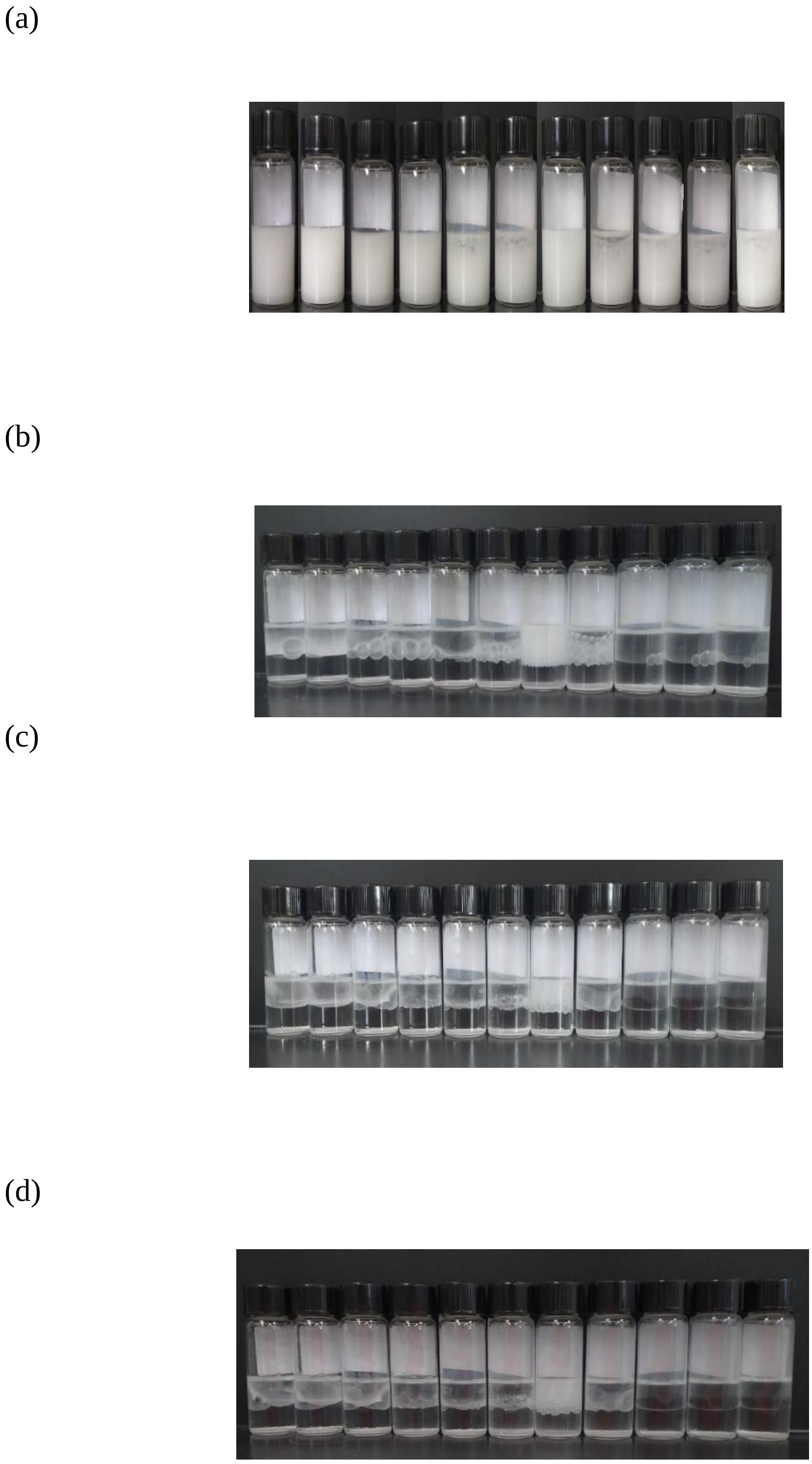


Figure 4.3. Appearance of o/w emulsions of 2 wt.% micron-sized silica particles originally dispersed in aqueous IL with octane (1:1 volume) for [IL]/M from left to right: 0, 3.9 × 10^{-4}, 1.56 × 10^{-3}, 6.25 × 10^{-3}, 1.25 × 10^{-2}, 2.5 × 10^{-2}, 5.0 × 10^{-2}, 1.0 × 10^{-1}, 2.0 × 10^{-1}, 3.0 × 10^{-1} and 4.0 × 10^{-1} at pH ~ 10 for (a) immediately after preparation, (b) after 24 h, (c) after 2 weeks and (d) after 3 weeks.

Figure 4.4 is a plot of stability to coalescence (f_o) as a function of IL concentration for o/w emulsions after 3 weeks. From the plot, at no IL concentration, the f_o value was at a maximum value of 1 and the emulsion formed was most unstable with complete phase separation. There was a sharp minimum at IL concentration of 5.0×10^{-2} M and f_o equal to 0. This IL concentration showed the formation of the most stable emulsions with complete stability to coalescence, hence $f_o = 0$. Afterwards, the values of f_o increased rapidly to the limit of 1 again at IL concentrations ranging from 1.0×10^{-1} M to 4.0×10^{-1} M, corresponding to maximum emulsion instability and complete phase separation of the emulsions formed.

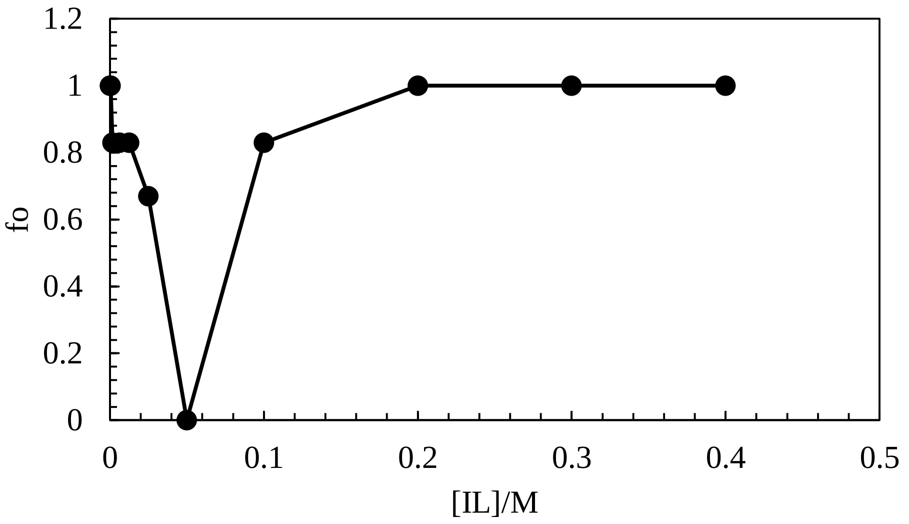


Figure 4.4. Plot of stability to coalescence (f_o) as a function of IL concentration for o/w emulsions of 2 wt. % micron-sized silica originally dispersed in water 3 weeks after preparation.

4.2.2 Particles originally dispersed in octane

Figure 4.5 shows the micrograph of micron-sized silica particles dispersed in octane. The hydrophilic particles can be seen to be dispersed more as clusters than discrete particles.

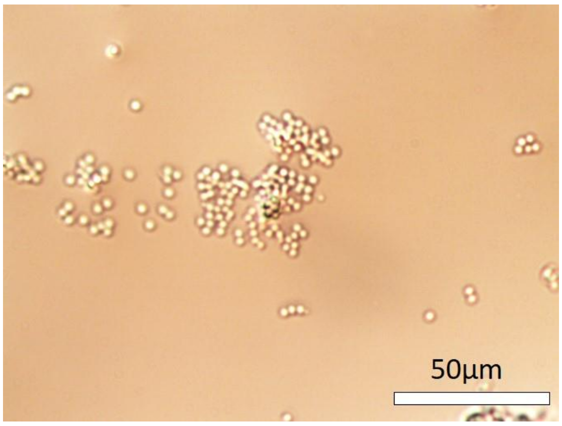


Figure 4.5. Micrograph of 2 wt. % micron-sized silica particles dispersed in octane.

The appearance of o/w emulsions for particles originally dispersed in octane for IL concentrations from 0 M to 4.5 × 10^{-1} M is shown in Figure 4.6. Stable emulsions were observed at IL concentrations from 0 to 5.0 × 10^{-2} M 24 h after preparation until 1 week after. This is in line with the work of Yang *et al*. who formed stable magnetically responsive IL-based Pickering emulsions using amphiphilic Fe3O4 nanoparticles particles and C4mim[PF6] as a hydrophobic IL [3]. Although the emulsion without IL completely phase separated after 1 week, emulsions at IL concentrations from 3.9 × 10^{-4} M to 5.0 × 10^{-2} M remained partially stable for up to 3 weeks although showing increased coalescence at higher concentrations.

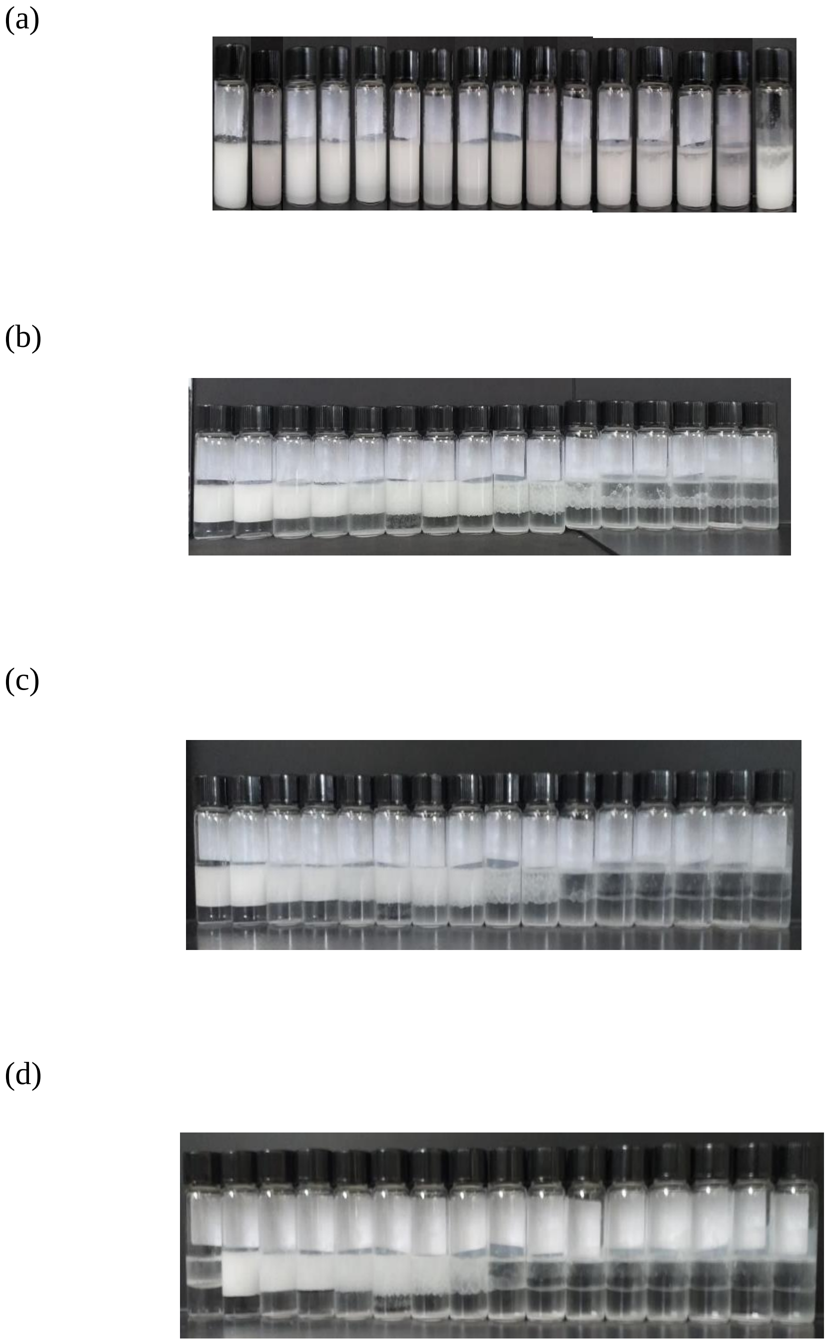


Figure 4.6. Appearance of o/w emulsions of 2 wt.% micron-sized silica originally dispersed in octane with aqueous IL (1:1 volume) for [IL]/M from left to right: 0, 3.9×10^{-4}, 1.56×10^{-3}, 3.13×10^{-3}, 6.25×10^{-3}, 1.25×10^{-2}, 2.5×10^{-2}, 5.0×10^{-2}, 1.0×10^{-1}, 1.5×10^{-1}, 2.0×10^{-1}, 2.5×10^{-1}, 3.0×10^{-1}, 3.5×10^{-1}, 4.0×10^{-1} and 4.5×10^{-1} at pH ~ 10 for (a) immediately after preparation, (b) after 24 h, (c) after 1 week, and (d) after 3 weeks.

A plot of f_o (stability to coalescence) versus IL concentration for time intervals from 0 to 3 weeks is shown in Figure 4.7. The plot shows that the emulsions were stable to coalescence at lower IL concentrations from 3.9×10^{-4} M to 5.0×10^{-2} M with an f_o value of 0 at 24 h, showing zero coalescence and maximum emulsion stability. Afterwards, coalescence and f_o values gradually increased with time as IL concentration increases until an extreme f_o value of about 1 was reached at [IL] from 1.0×10^{-1} M to 4.5×10^{-1} M within 1 to 3 weeks, resulting in increased emulsion instability. Comparing this with when particles were originally dispersed in water, originally dispersing the particles in oil activates more of the silica particles to adsorb at the oil-water interface.

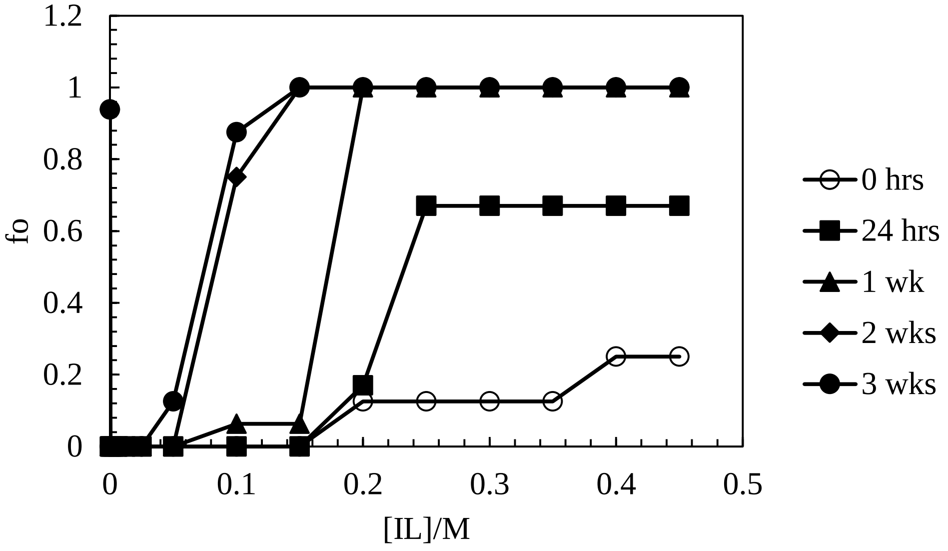


Figure 4.7. Plot of f_o *versus* IL concentration for o/w emulsions of 2 wt. % micron-sized silica originally dispersed in octane at 0 to 3 weeks after preparation.

Figure 4.8 shows optical microscopy images of o/w emulsions 3 weeks after preparation. From the images, the lower IL concentrations show more o/w emulsion droplets than the higher IL concentrations, suggesting increasing emulsions coalescence with increasing IL concentration. Also, at higher magnifications, most of the images show close packed particles around oil drops. This indicates that the micro-sized silica particles really stabilised the emulsions while the IL served as an adsorbing surfactant.

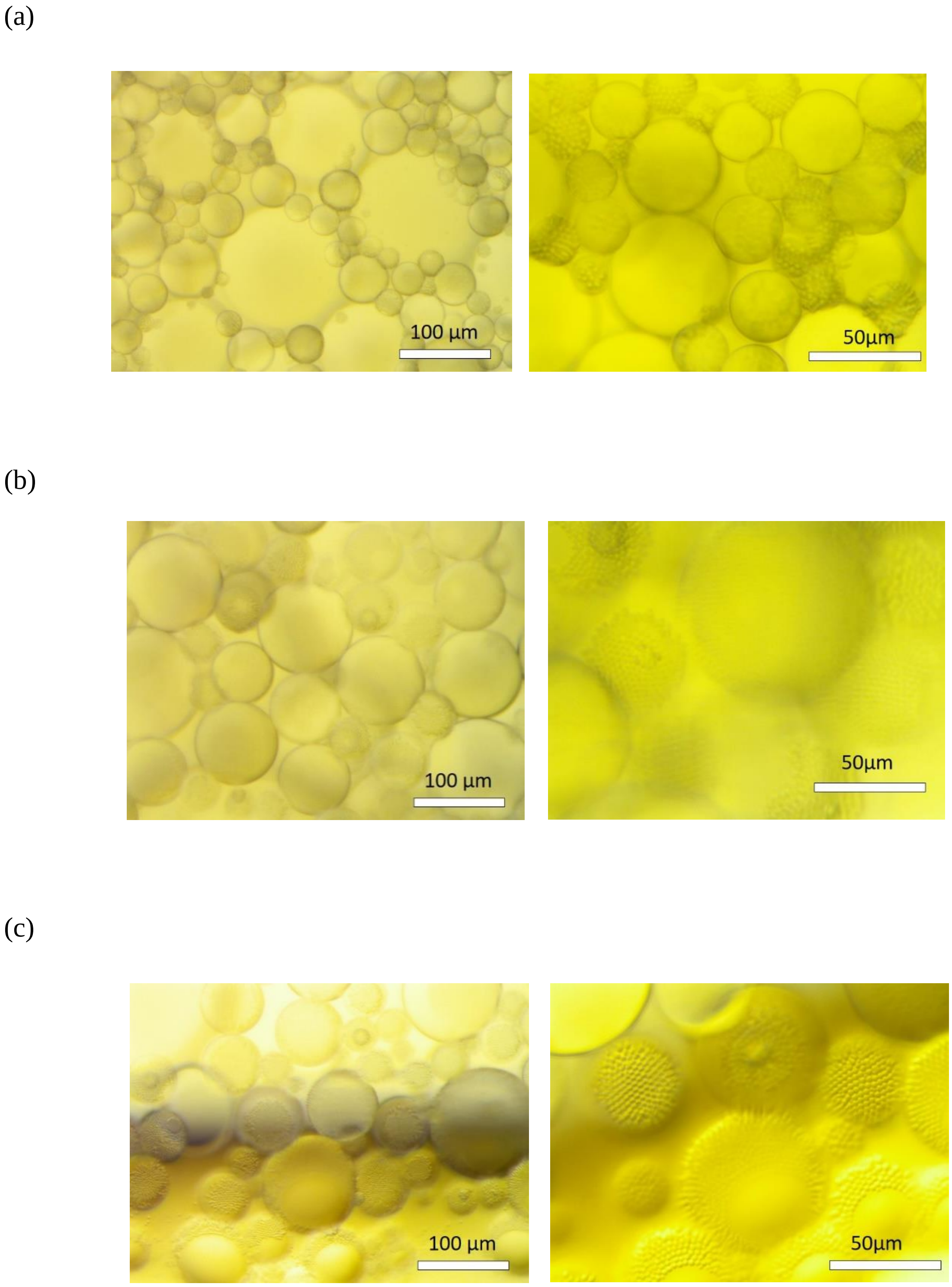


Figure 4.8. Optical microscopy images of some stable o/w emulsions of 2 wt.% micron-sized silica originally dispersed in octane at 3 weeks for IL concentrations from top to bottom of (a) 3.9×10^{-4} M, (b) 1.56×10^{-3} M, and (c) 3.13×10^{-3} M at different magnifications.

Figure 4.9 is a plot of the average drop diameter as a function of IL concentration for stable o/w emulsions 3 weeks after preparation. The average drop diameter can be seen to increase from 59 µm to 86 µm at IL concentrations from 3.9×10^{-4} M to 1.56×10^{-3} M before recording a steady and gradual decrease to 47 µm as the IL concentration increases to 1.25×10^{-2} M. At higher IL concentrations above 1.25×10^{-2} M, the average drop diameter could not be determined because of increased and obvious emulsion coalescence. The increase in emulsion instability could be ascribed to rise in the interfacial resistance from the high concentration of the IL at the interface.[4]

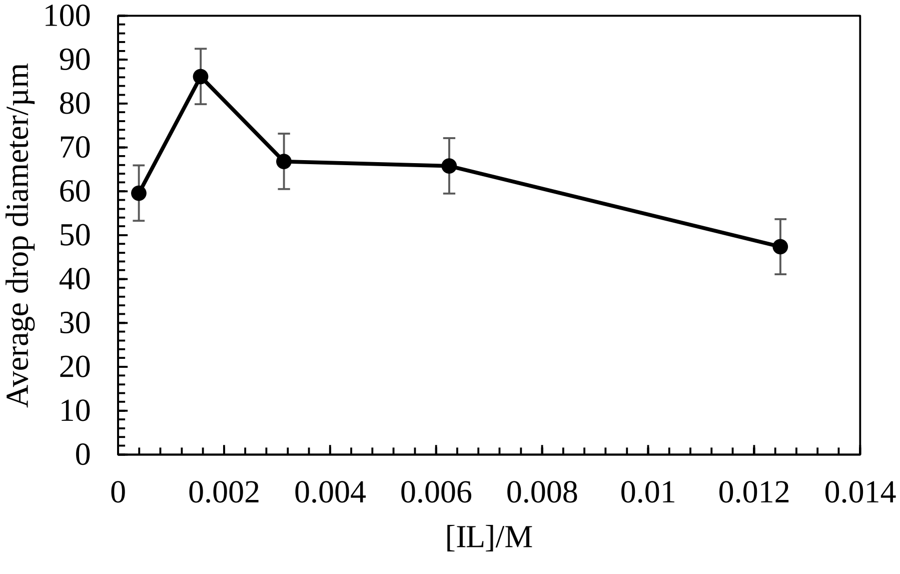


Figure 4.9. Plot of average drop diameter *versus* [IL] for stable o/w emulsions of 2 wt. % micron-sized silica originally dispersed in octane 3 weeks after preparation.

4.2.3 Powdered particle method

The appearance of o/w emulsions prepared using the powdered particle method for IL concentrations from 0 M to 4.0×10^{-1} M is shown in Figure 4.10. IL concentrations from 0 M to 5.0×10^{-2} M produced stable emulsions up to 24 hours while the higher IL concentrations from 2.0×10^{-1} M to 4.0×10^{-1} M exhibited complete phase separation 24 h after preparation. For the stable emulsions, there was gradual but increasing coalescence as IL concentration increases up to 3 weeks except for the two lowest concentrations of 0 M and 3.9×10^{-4} M, which remained stable for the whole 3-week period. The vial without IL that formed stable emulsions represents a major deviation from what was observed in the previous two methods of preparation. This deviation shows that the emulsion was solely stabilized by the silica particles in the absence of the IL as an adsorbing surfactant. This is in line with the prepositions of Chevalier et al and Tambe et al, where nanoparticles, in this case, silica micron-sized particles, can be used to modify the rheological properties of liquid-liquid interfacial region in emulsions, thus serving as a direct replacement for surfactant and be used as a solid emulsifier [5] in stabilising Pickering emulsions [6, 7] . The other stable emulsions containing IL agrees with the works of Binks et al, who reported the successful preparation of novel stable emulsions which contain ionic liquids and exclusively stabilised by silica nanoparticles [8, 9].

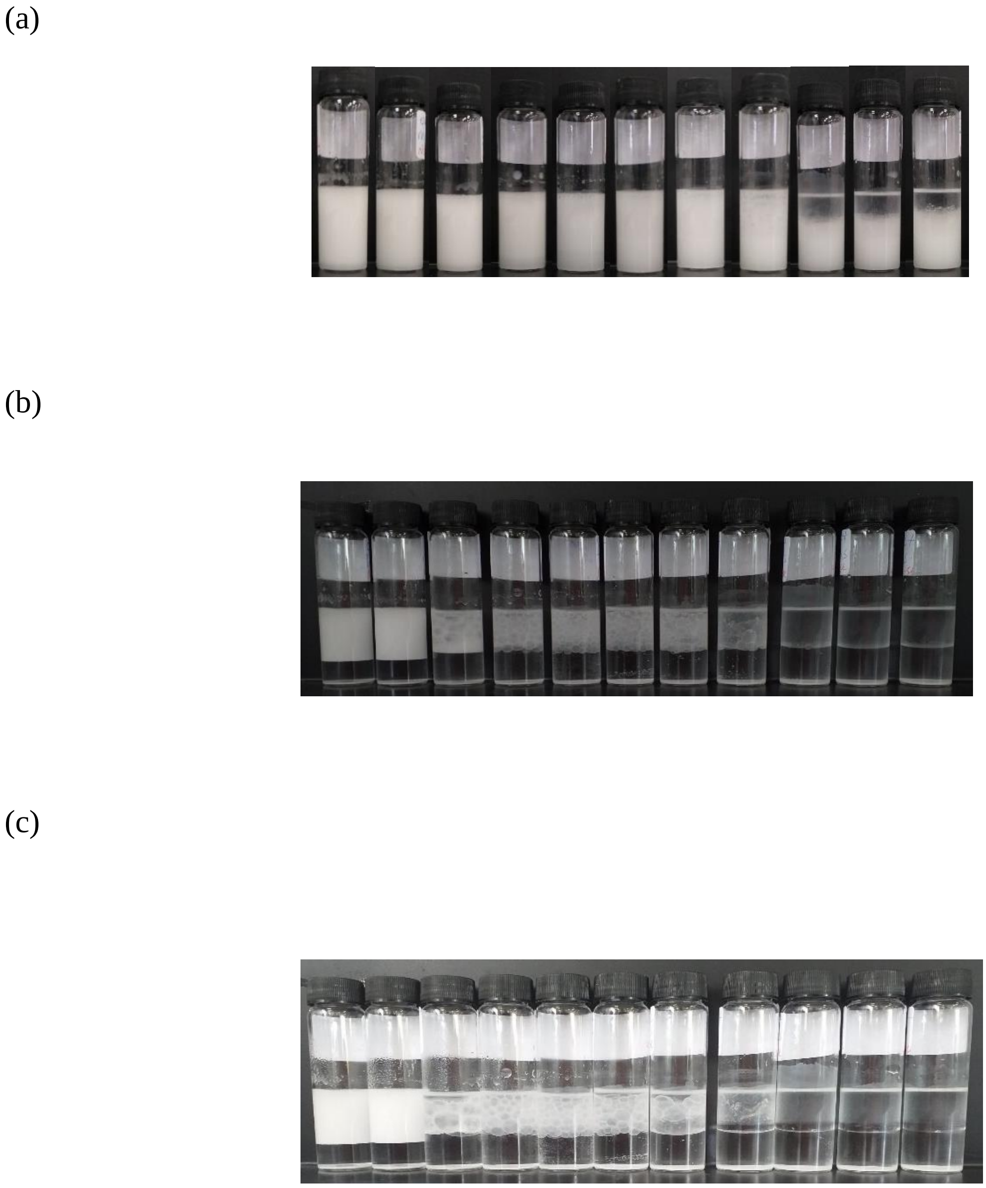


Figure 4.10. Appearance of o/w emulsions prepared with 2 wt.% micron-sized silica and the powdered particle method with aqueous IL and octane (1:1 volume) for [IL]/M from left to right: 0, 3.9×10^{-4}, 1.56×10^{-3}, 6.25×10^{-3}, 1.25×10^{-2}, 2.5×10^{-2}, 5.0×10^{-2}, 1.0×10^{-1}, 2.0×10^{-1}, 3.0×10^{-1} and 4.0×10^{-1} at pH ~ 10 (a) immediately, (b) 24 h, (c) 3 weeks after preparation.

Figure 4.11 is a plot of f_o as a function of IL concentration for o/w emulsions prepared by the powdered particle method. Emulsions possess an f_o value of about 0 and were very stable to coalescence at low IL concentrations of 0 M to 3.9×10^{-4}M. However, with time, the emulsion stability to coalescence decreased drastically with increasing IL concentration from 1.56×10^{-3} M to 4.0×10^{-1} M, up to a maximum f_o value of 1 as a result of complete phase separation,

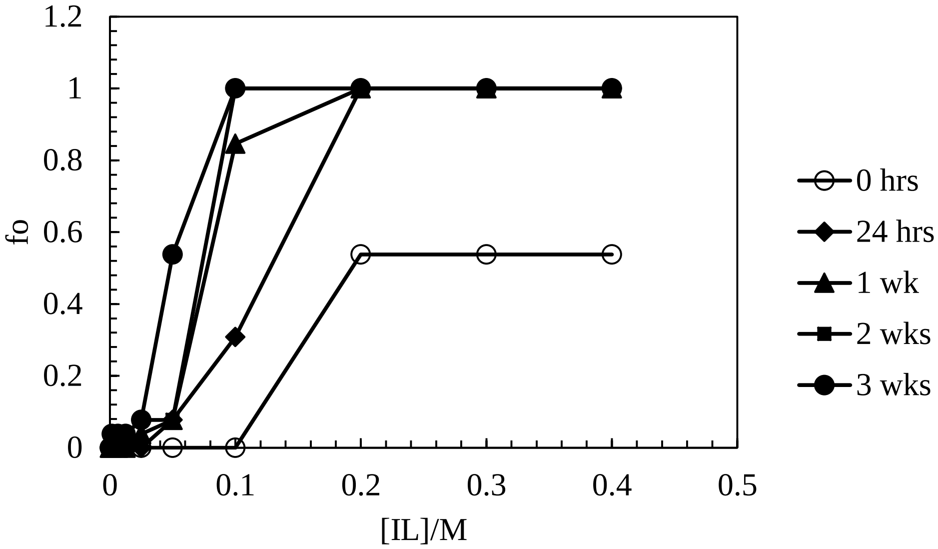
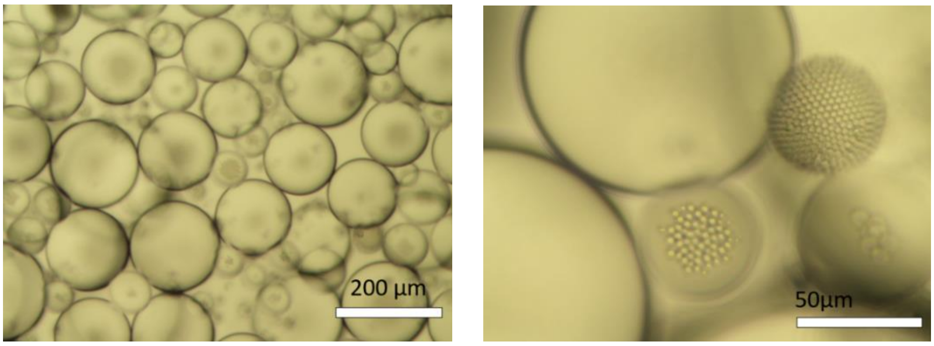


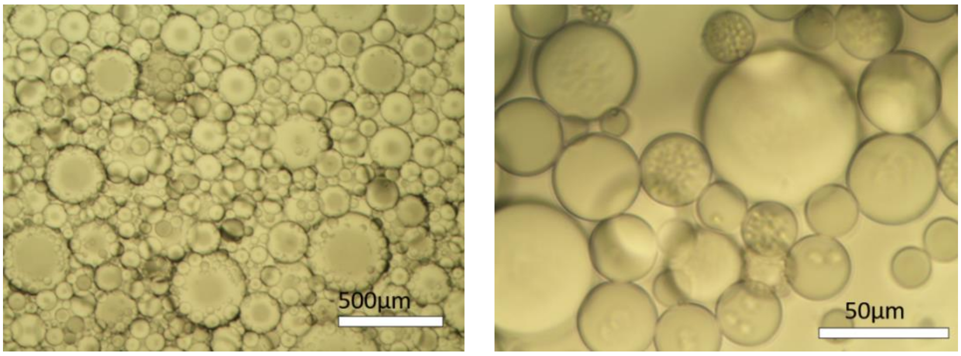
Figure 4.11. Plot of f_o as a function of IL concentration for o/w emulsions prepared by the powdered particle method of 2 wt. % micron-sized silica at 0 to 3 weeks after preparation.

Figure 4.12 shows the optical microscopy images of stable o/w emulsions at 3 weeks. The oil droplets appeared more closely packed together, with fewer spaces in-between at lower IL concentration and more loosely packed as the IL concentration increases, confirming increasing emulsion coalescence at higher IL concentrations. At higher magnifications, the particles can be seen on the surface of the oil drops, stabilising the droplets. This affirms that the IL can indeed serve as an adsorbing surfactant in Pickering emulsions stabilised by micro-sized silica particles even with the powdered particle method.

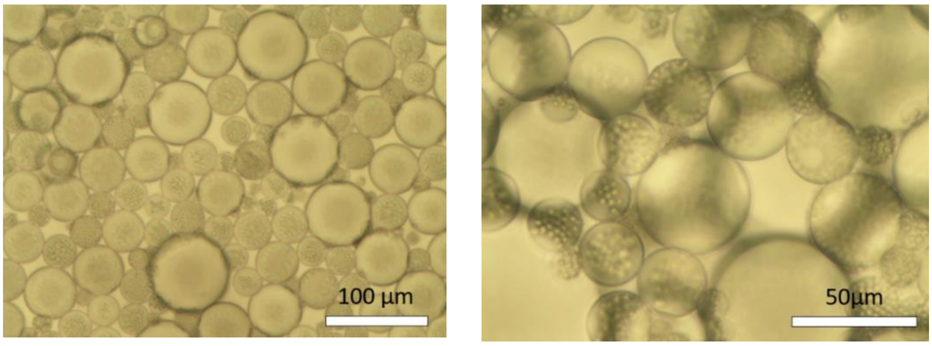
(a)



(b)



(c)



(d)

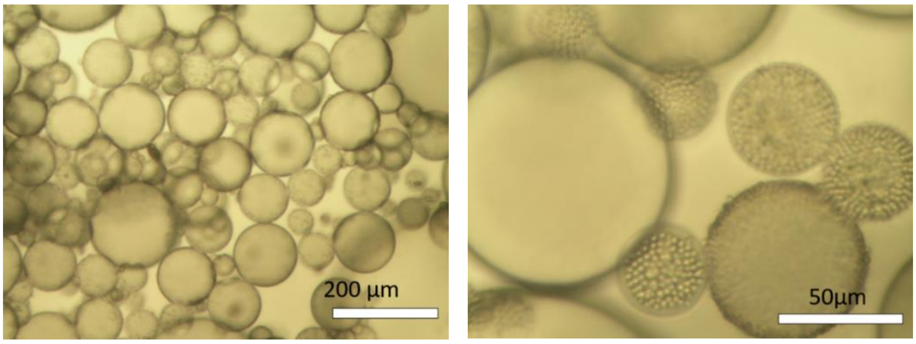


Figure 4.12. Optical microscopy images o/w emulsions prepared using the powdered particle method at 3 weeks for IL concentrations from top to bottom of (a) 0 M, (b) 3.9 × 10^{-4} M, (c) 1.56 × 10^{-3} M and (d) 6.25 × 10^{-3} M at different magnifications.

4.3 Effect of particle concentration at fixed [IL]

The effect of varying the particle concentration on emulsions stabilised by micron-sized silica particles was studied at fixed IL concentration. Two IL concentrations were investigated, which are 1.56 × 10^{-3} M and 1.25 × 10^{-2} M while varying the particle concentration from 0 to 4 wt.%. The particles were originally dispersed in octane. Having established from previous experiments that the IL can act as an adsorbing surfactant at low concentrations in emulsions stabilised by silica particles, two of such low concentrations of the IL where stable o/w emulsions formed were selected for use.

4.3.1 Effect of particle concentration at constant [IL] = 1.56 × 10^{-3} M

The appearance of o/w emulsions at a constant IL concentration of 1.56 × 10^{-3} M while varying the particle concentration is shown in Figure 4.13. As expected, the emulsion without particles underwent complete phase separation a few seconds after preparation because of absence of an emulsifier or particle as a surfactant.[5, 10] There was formation of o/w emulsions for the other particle concentrations. However, when the particle concentration was less than 1.5 wt. %, the rate of coalescence was high and the emulsions formed at was less stable. This can be attributed to the particles not being sufficient enough to effectively cover the droplets and stabilise the emulsions. However, more stable emulsions formed from particle concentration of 1.5 wt. % and above, with decreasing coalescence and increasing emulsion stability as particle concentration increases. This suggests that as the concentration of the particles increases, more particles adsorb at the octane-water interface, creating wider coverage of particles and increasing emulsion stability. This is similar to the findings of Li et al in their investigation of the influence of particle concentration on the stability of Pickering emulsions. From their findings, increase in particle concentration makes more particles to adsorb at the interface, forming single or multi-layer structure, thus stabilising the emulsions by preventing coalescence. The only difference is that Li et al worked with food-grade nanoparticles [11, 12].

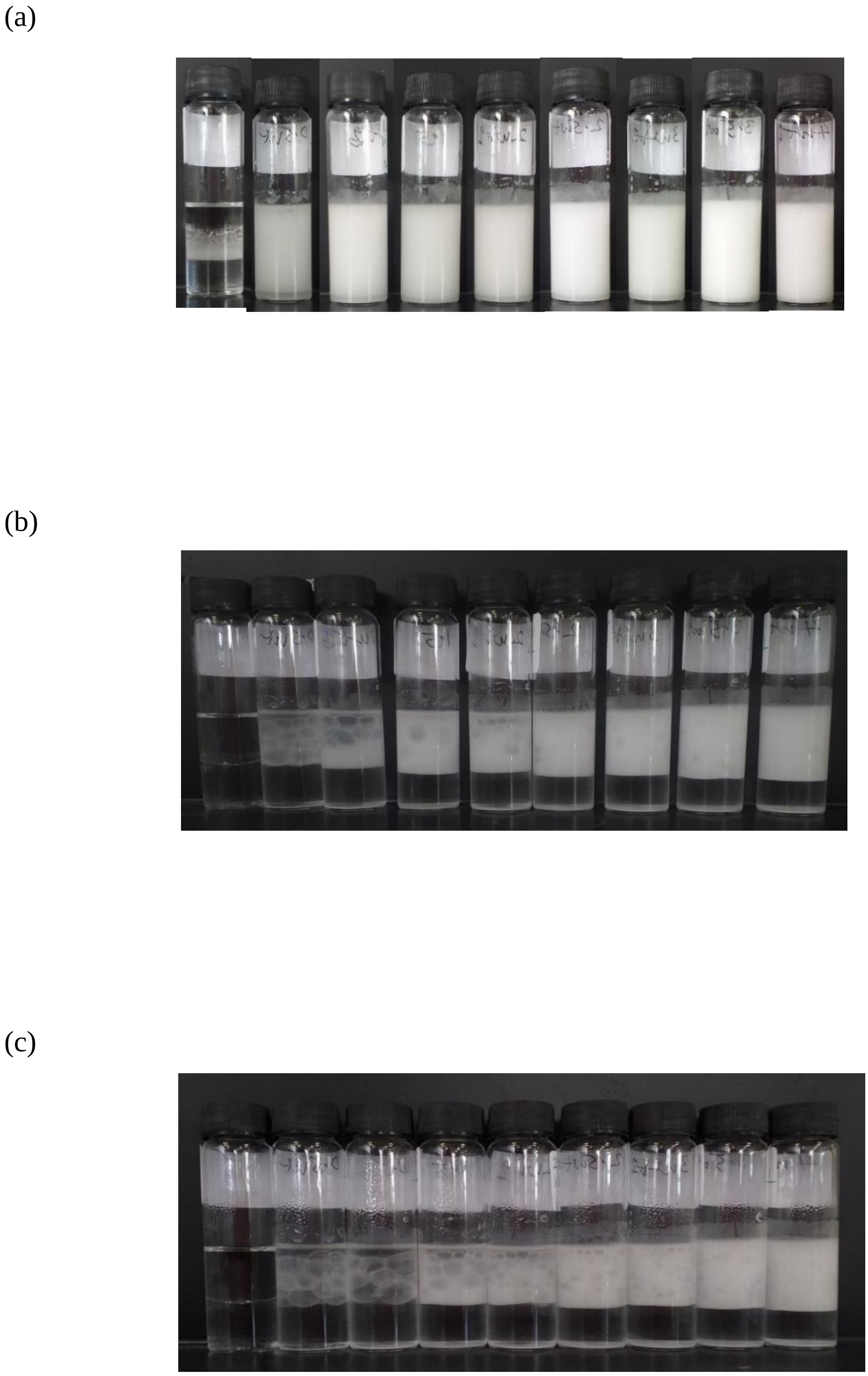
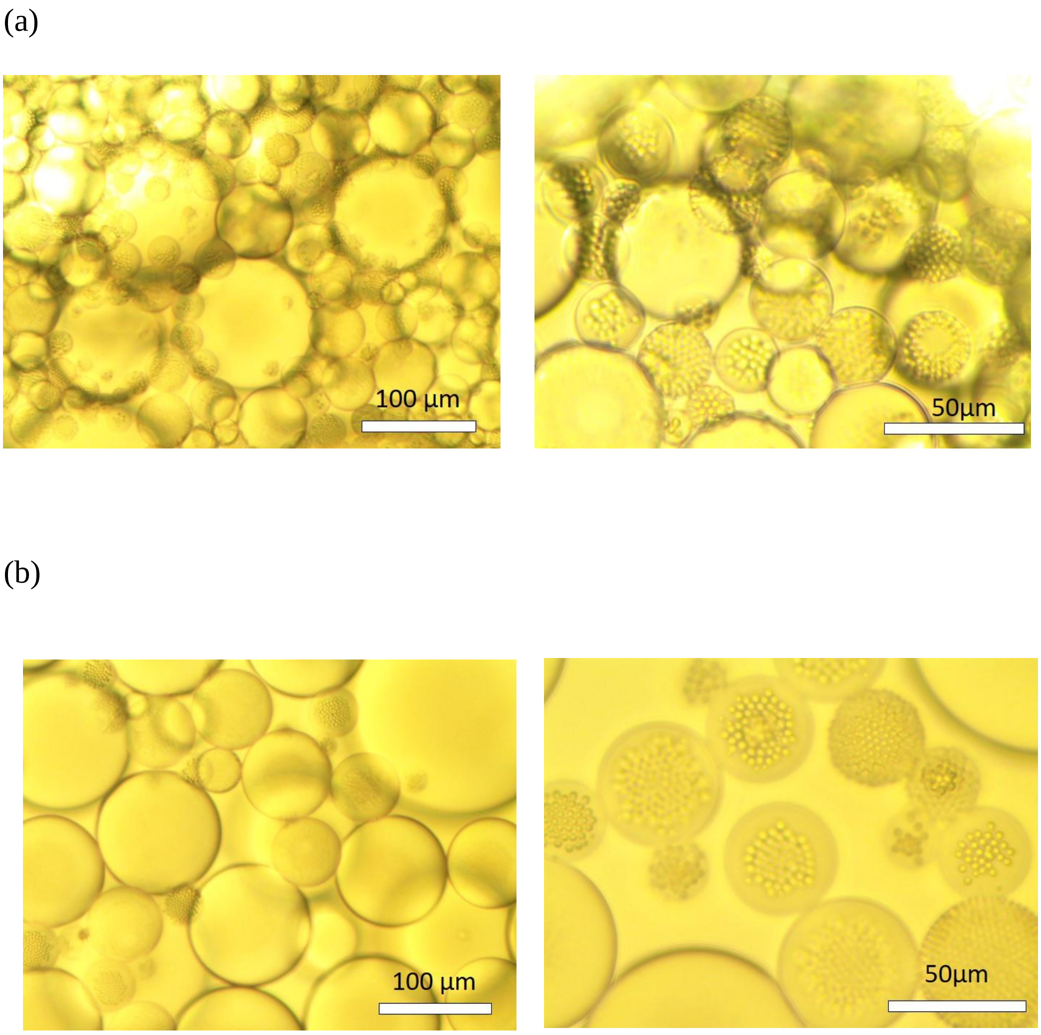


Figure 4.13. Appearance of o/w emulsions at constant [IL] of 1.56×10^{-3} M and varying concentration (wt.%) of micron-sized silica particles originally dispersed in octane from left to right of 0, 0.5, 1, 1.5, 2, 2.5, 3, 3.5 and 4 at pH ~ 10 (a) immediately, (b) 48 h and (c) 3 weeks after preparation.

The optical microscopy images at 3 weeks of the stable o/w emulsions are shown in Figure 4.14. At higher magnification, the micron-sized silica particles are seen to adsorb on the surface of the oil drops as they stabilise the emulsions. There was no obvious difference observed in the micrographs at the different particle concentrations except in terms of the average drop diameter, which increased a little before gradually dropping in value. This varies with what was expected, which is for the drop size to decrease to a limit and the density of interfacial particles to increase [13, 14].



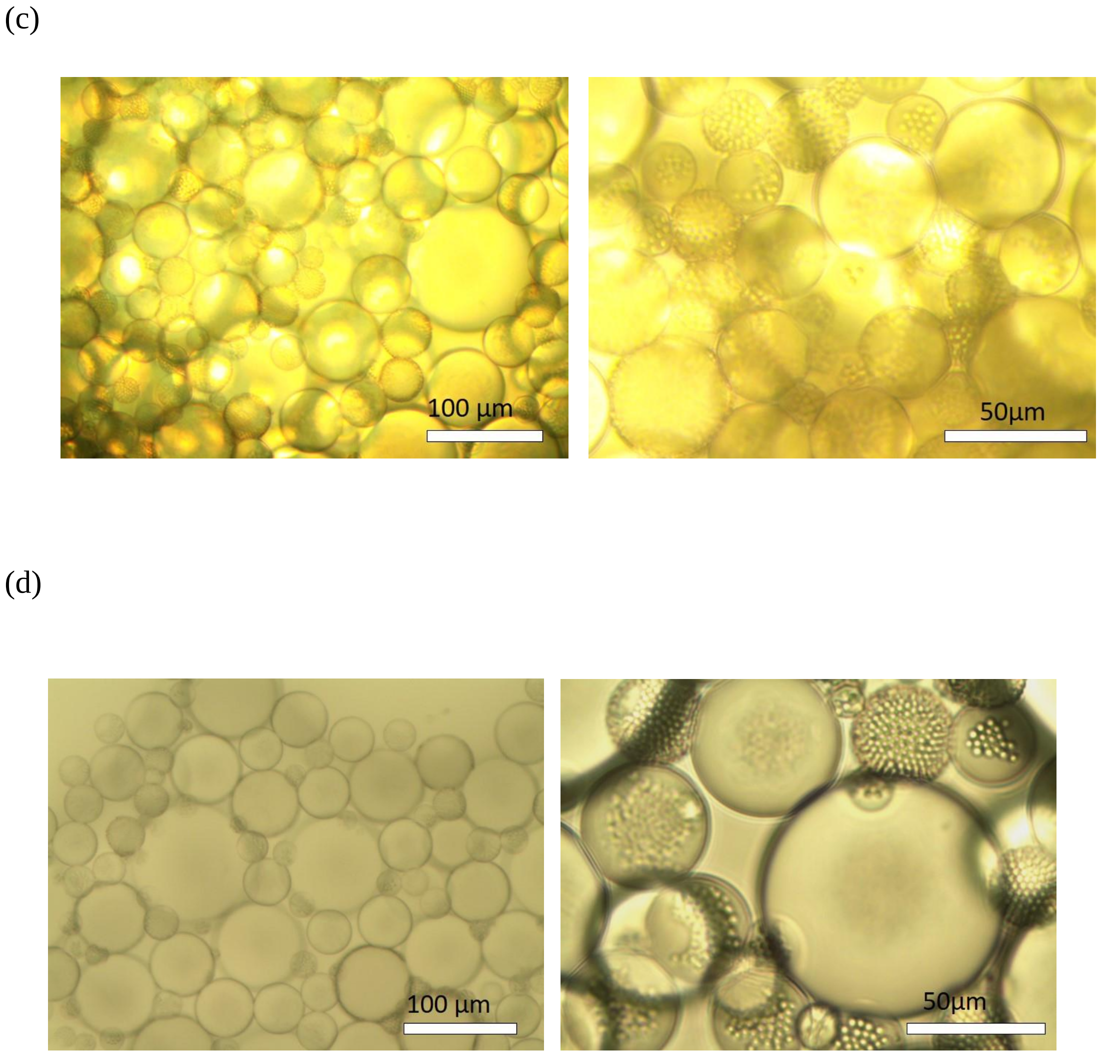


Figure 4.14. Optical microscopy images at 3 weeks of o/w emulsions at constant [IL] of 1.56×10^{-3} M and varying micron-sized silica particle concentration (wt.%) at (a) 1.5, (b) 2, (c) 2.5, and (d) 4 at different magnification.

The plot of the average drop diameter *versus* particle concentration at fixed IL concentration of 1.56×10^{-3} M at 3 weeks is shown in Figure 4.15. The average drop diameter is shown to increase from about 38 µm to 67 µm as the micron-sized silica particle concentration increases from 1.5 wt. % to 2 wt.%, before it gradually and continuously dropped to about 39 µm with increasing particle concentration. The steady decrease in average drop diameter can be attributed to the creation of larger interfacial area when more silica particles were added as the concentration increased [14-17]. This is in line with what was expected and reported in literature, where average drop diameter decreases with increasing particle concentration, leading to increase in emulsion stability [13-16].

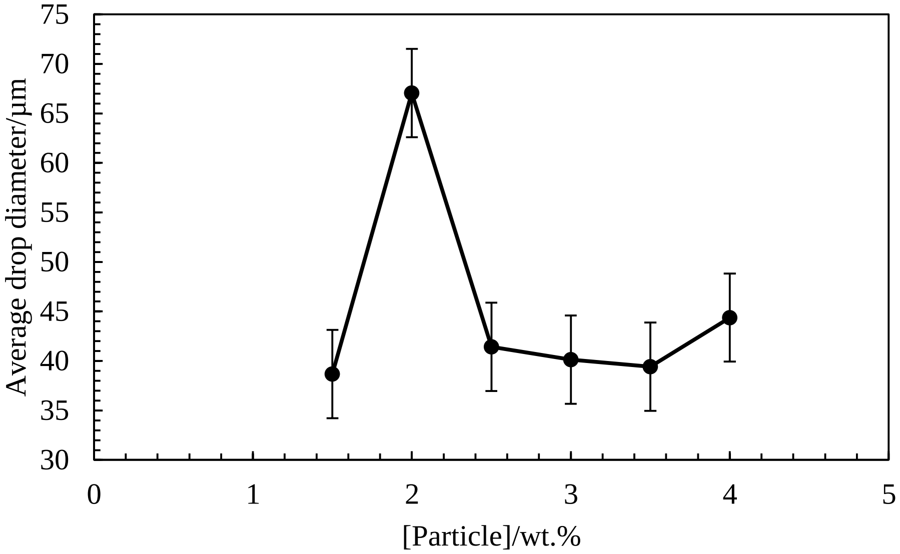


Figure 4.15. Plot of the average drop diameter *versus* micron-sized silica particle concentration at fixed IL concentration of 1.56×10^{-3} M at 3 weeks.

4.3.2 Effect of particle concentration at constant [IL] = 1.25×10^{-2} M

Figure 4.16 shows the appearance of o/w emulsions at constant IL concentration of 1.25×10^{-2} M while varying the particle concentration from 0.5 to 4 wt.%. Unlike the stable o/w emulsions formed at lower IL concentration the emulsions formed were less stable to coalescence. Hence, at particle concentrations of 0.5, 1 and 1.5 wt.%, emulsions almost completely phase separated a few minutes after preparation while at higher particle concentrations from 2 to 4 wt.%, the emulsions showed increasing stability to coalescence. However, optical microscopy analysis at 3 weeks after preparation did not show any obvious emulsion droplets for all the particle concentrations studied due to obvious coalescence at this time. This suggests that increase in the concentration of the IL leads to a decrease in emulsion stability due to a rise in the interfacial resistance from the excess IL ions at the interface.[4]

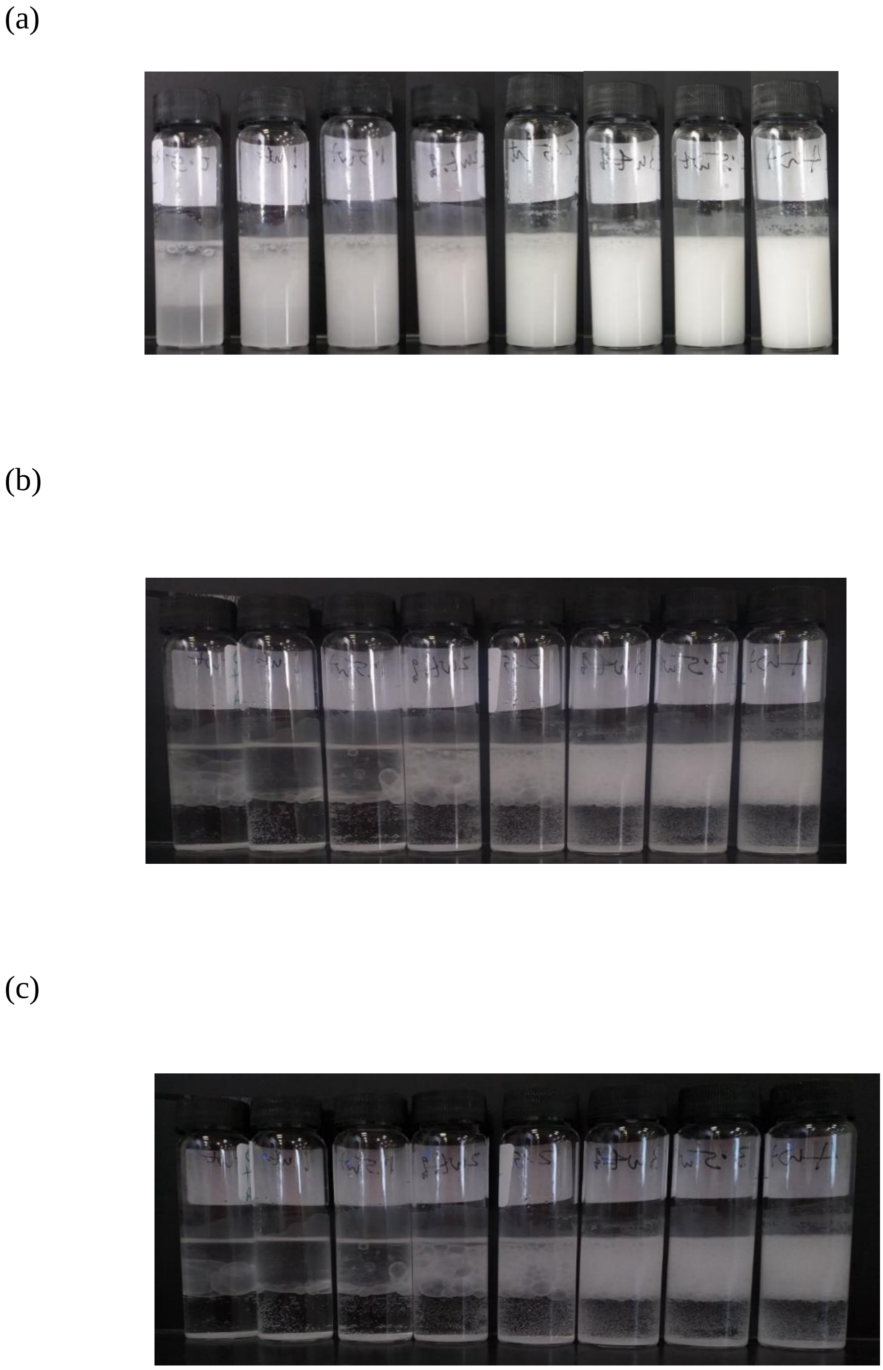


Figure 4.16. Appearance of o/w emulsions at constant IL of 1.25×10^{-2} M and varying concentration (wt.%) of micron-sized silica particles originally dispersed in octane from left to right of 0.5, 1, 1.5, 2, 2.5, 3, 3.5 and 4 wt.% (1:1 volume) at pH ~ 10 (a) immediately, (b) 48 h and (c) 3 weeks after preparation.

4.4 Comparison between the respective results from studies of silica nanoparticles and micron-sized silica particles

Considering the dispersion studies, Ludox HS-30 silica nanoparticles formed visually stable aqueous dispersions in aqueous IL without sedimentation of the particles unlike its nanoparticle counterpart, Ludox CL, which formed unstable aqueous dispersions with some sedimentation at higher IL concentrations. On the other hand, the aqueous dispersions of micron-sized silica in aqueous IL formed sedimentation at all the IL concentrations studied. The obvious sedimentation of micron-sized silica particles at all the IL concentrations studied can be attributed to the larger particle size compared to the nanoparticles.

For the emulsion studies, both the Ludox HS-30 silica nanoparticles and micro-sized silica particles formed stable o/w emulsions at some IL concentrations while the Ludox CL silica nanoparticles formed unstable emulsions at all the IL concentrations studied.

4.5 Conclusions

The use of the ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate (IL) as an adsorbing surfactant in emulsions stabilised by micron-sized silica particles was investigated. Three different methods were used to introduce the particles before homogenisation. They include dispersing particles originally in water, dispersing particles originally in oil (octane) and the powdered particle method. The effect of varying the particle concentration at constant IL concentration was also examined.

When the particles were originally dispersed in water, stable o/w emulsions were only seen at an intermediate IL concentration of 5.0×10^{-2} M, while both the lower and higher IL concentrations recorded unstable emulsions with partial to complete phase separation.

Originally dispersing the particles in octane gave more stable o/w emulsions at lower IL concentrations from 3.9×10^{-4} M to 5.0×10^{-2} M, while unstable emulsions with increasing coalescence was observed at higher IL concentrations from 1.0×10^{-1} M to 4.5×10^{-1} M. Thus, when particles are originally dispersed in octane, it activates more of the silica particles to adsorb at the octane-water interface than when they are originally dispersed in water.

The powdered particle method gave results similar to when particles were originally dispersed in octane, except that the emulsion formed without IL remained stable for the 3 weeks of observation with no coalescence.

Varying the particle concentration at constant IL concentration produced more stable o/w emulsions at a lower IL concentration of 1.56×10^{-3} M than at 1.25×10^{-2} M. This aligns with the earlier observation that emulsion stability decreases with increasing IL concentration. Therefore, the IL, 1-ethyl-3-methylimidazolium tetrafluoroborate, can act as an adsorbing surfactant to increase the stability of o/w emulsions stabilised by 2 micron-sized silica at lower IL concentrations.

4.6 REFERENCES

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Chapter 5

5.0 Conclusion and future work

5.1 Conclusions

The use of ionic liquid as an adsorbing surfactant in a mixture of octane and water was investigated in this thesis. Pickering emulsions stabilised by silica particles, both nanoparticles and micron-sized silica particles, were prepared and used in the investigations. Chapter 3 of the thesis researched on the aqueous dispersion of silica nanoparticles in ionic liquid and emulsion studies using silica nanoparticles as the stabilizer. The ionic liquid, 1-ethyl-3-methylimidazolium tetrafluoroborate is the adsorbing surfactant. On the other hand, investigations in Chapter 4 used micron-sized silica particles as the stabilizer and it employed different methods to disperse the silica particles prior to homogenisation. Findings showed that the ionic liquid used can indeed serve as an adsorbing surfactant in Pickering emulsions stabilised by silica particles.

Chapter 3 explored aqueous dispersions of silica nanoparticles in aqueous ionic liquid using colloidal silica nanoparticles, Ludox CL, positively charged at low pH of about 3.6 and Ludox HS-30, negatively charged at higher pH of about 10. The Ludox CL formed cloudy aqueous dispersions at lower ionic liquid concentrations and had sedimentations of silica particles at higher concentrations of the ionic liquid. Hence, the Ludox CL dispersions in aqueous ionic liquid were unstable, with decrease in stability as the ionic liquid concentration increases. However, the Ludox HS-30 dispersions in ionic liquid was less cloudy, with no sedimentations of silica particles at all the ionic liquid concentrations studied. Therefore, the Ludox HS-30 dispersions in ionic liquid were stable.

Both Ludox CL and Ludox HS-30 dispersions were characterised using dynamic light scattering for zeta potential and particle size measurements. The results showed that as the IL concentration rises, there was change in the zeta potential values for Ludox CL from +34 mV to reduced negative values and reduced positive values, suggesting decrease in the stability of the dispersions with increase in the concentration of the IL. For the Ludox HS-30, the zeta potential values changed from -30 mV to lower negative values with increase in ionic liquid concentration, showing decrease in dispersion stability. There was rise in the particle size with increase in IL concentration for both Ludox CL and Ludox HS-30, suggesting particle aggregation and less stability of the dispersions.

The investigations of the colloidal silica nanoparticle emulsions confirmed the findings of the dispersion studies, where Ludox CL formed unstable o/w emulsions at all the IL concentrations investigated while Ludox HS-30 formed stable o/w emulsions at intermediate IL concentrations from 2.5×10^{-2} M to 2.0×10^{-1} M.. Therefore, the anion of the Ludox HS-30 can be said to modify the cation of the ionic liquid while the cation of the Ludox CL cannot be said to modify the anion of the IL.

Chapter 4 experimented on ionic liquid as the adsorbing surfactant in Pickering emulsions stabilised by micron-sized silica particles using three methods to disperse the silica particles before homogenisation. The methods are the particles originally dispersed in water, particles originally dispersed in octane and the powdered particle method, where there is a simultaneous addition of octane and water to the particles. The concentration of silica particles was kept constant at 2 wt. % while varying the concentration of the ionic liquid in the aqueous medium from 0 to 4.5×10^{-1} M. Also, emulsion studies were done at constant IL concentrations of 1.56×10^{-3} M and 1.25×10^{-2} M while varying the concentrations of the silica particles from 0 to 4 wt. %. Stable o/w emulsions were formed at IL concentrations from 3.9×10^{-4} M to 5.0×10^{-2} M for both the powdered particle method and when the particles were originally dispersed in octane, while unstable o/w emulsions were observed when particles were originally dispersed in water except at IL concentration of 5.0×10^{-2} M.

When the IL concentration was kept constant and the particle concentration varied, more stable o/w emulsions were formed at the lower IL concentration of 1.56×10^{-3} M than at 1.25×10^{-2} M. Optical microscopy of the stable o/w emulsions showed the micron-sized silica particles sitting on the droplets and stabilizing the emulsions.

The findings show that the IL can act as an adsorbing surfactant in Pickering emulsions stabilized by Ludox HS-30, micro-sized silica particles initially dispersed in octane and the powdered particles method but could not act as an adsorbing surfactant when the micron-sized silica particles were originally dispersed in water.

5.2 Future work

Suggestions on further investigations for future work are as follows.

Equal volumes of oil and water was used in this thesis. Future work could explore varying the volume ratio of the oil and water phase to 20:80, 30:70, 40:60, and vice versa. Octane could be replaced with other non-hazardous environmentally friendly oils such as soybean oil or olive oil, to enhance the application in food industries.

Also, other types of imidazolium-based IL could be used and the length of the alkyl chain increased, such as 1-butyl-3-methyl, 1-octyl-3-methyl, and 1-decyl-3-methyl. In a similar twist, either the anion or the cation of the IL could be changed and its effect as an adsorbing surfactant in stabilising emulsions investigated.

Additional suggestions include investigating the stabilisation of Pickering emulsions using other particles such as alumina, clay and pollens, with the same or a different IL as the adsorbing surfactant. These possible further studies will increase the applications of Pickering emulsions in surface electroplating, ceramics, forensics and related industries.