Cape Peninsula
University of Technology

MANUFACTURE AND STABILISATION OF HIGHLY CONCENTRATED EMULSIONS USING POLYHEDRAL OLIGOMERIC SILSESQUIOZANE NANOMOLECULES

by

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Thesis submitted in fulfilment of the requirements for the degree

Master of Technology: Chemistry

in the Faculty of Science

at the Cape Peninsula University of Technology

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Cape Town
December 2015

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ABSTRACT

The subject of this current study concerns highly concentrated emulsions of the explosive grade. A distinguishing characteristic of these systems is a high internal to external phase volume ratio. The volume fraction of the aqueous phase of such an emulsion generally far exceeds the close packing limit. Continuous phase of the system is a supersaturated aqueous solution of ammonium nitrate inorganic salt. In combination with high internal phase concentration, this inevitably leads to the destabilisation of the system. The thermodynamic instability of such systems is attributed to two major factors: 1) crystallisation of dispersed phase and 2) coalescence of the individual droplets within the bulk. This poses a significant problem since destabilisation of the bulk emulsion in turn leads to partial or complete loss of sensitivity to detonation of the final product of which highly concentrated emulsion is the base.

Since the invention of such types of bulk explosives, a considerable and on-going effort has targeted the improvement of the stability of these systems, with a scope primarily focused on the use of various surfactant agents with different properties as well as stabilising mixtures containing numerous surfactants. In recent years, a new approach has been explored: the stabilisation of highly concentrated emulsions with the use of solid fumed silica nanoparticles. This is a promising new field of study, already being implemented by manufacturers and actively developing.

The focus of this present study is to investigate and lay the ground work for further research in the principally new approach towards the stabilisation of highly concentrated emulsions with the use of the polyhedral oligomeric silsesquiozane nanomolecules. These are unique compounds possessing hybrid inorganic-organic structures and properties, and carrying a range of advantages over currently implemented surfactants. As opposed to silica nanoparticles, these compounds are not solid particles but can be regarded as molecular silica.

This investigation will focus on the general possibility of implementation of such compounds as stabiliser agents for emulsions in general, and highly concentrated emulsions of the explosive grade in particular, and the resultant effects on the stability. Effects on stability will be investigated both when used solely and in combination with common surfactants. In

addition, stability both on shelf and under stress will be investigated within the framework of the study.

ACKNOWLEDGEMENTS

I would like to thank the following persons and organisations for their contributions towards the completion of this thesis:

First and foremost my beloved parents, without whom none of this would be possible. For the gift of life, love, constant support, guidance and encouragement throughout this life. For all the endless patience and for making me the person I am.

Prof. Irina Masalova and Prof. Bhekumusa Ximba for their professional guidance and supervision throughout the whole research process.

Dr. Neda Sanatkaran, a dear friend and colleague, for all the help, support, guidance and encouragement on this journey.

Mr Nazeem George, my laboratory supervisor, for his assistance, help, advice, patience and for providing a pleasant and safe environment for conducting research.

AEL Mining Services for providing the financial backbone and bulk of the materials used in the study.

Cape Peninsula University of Technology as well as the Flow Process Research Centre for providing the facilities to conduct the research.

Last but not least, I would like to extend my thanks to my friend Adam for being there for me in good and bad on every step of this venture.

DEDICATION

This work is dedicated to my dear parents whom I love endlessly.

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GLOSSARY

Terms	**Explanation**
Coalescence	Spontaneous joining of smaller droplets in an emulsion system to form larger droplets
Crystallisation	Destabilisation mechanism due to a change in the physical state of the emulsion dispersed phase – change from liquid state to crystal state
Elasticity/Elastic modulus	A modulus of a body that obeys Hook’s law
Emulsion	Two immiscible liquids (usually oil and water), with one of the liquids dispersed as small spherical droplets in the other
Explosive emulsion	High internal phase water-in-oil emulsion of a concentrated solution of nitrate salts in water emulsified in an oil base
Interfacial tension	Measurement of cohesive (excess) energy present at an interface arising from the imbalance of forces between molecules at an interface (gas/liquid, liquid/liquid, gas/solid, liquid/solid)
Interaction parameter	An indicator which compares the molecular interaction of surfactant mixtures with the self-interactions of surfactants individually before mixing
Modulus	The quotient of stress and strain where the type of stress and strain is defined by the type of deformation employed
Rheology	Science of deformation and flow of matter, relevant to

	the deformation of materials resulting from an applied stress
Shear	The relative movement of parallel adjacent layers
Surfactant	An amphiphilic (amphipathic) molecule that has a hydrophilic head group (polar region), with a high affinity for water, and a lipophilic tail group (non-polar region), with a high affinity for oil
Viscoelastic	A time-dependent property in which a material under stress produces both a viscous and an elastic response
Viscosity	The property of a material to increasingly resist deformation as the shear rate increases; a measure of this property is defined as the quotient of shear stress divided by the shear rate in steady flow
Yield stress	A critical shear stress value below which an ideal plastic or viscoplastic material behaves as a solid (no flow). Once the yield stress is exceeded, a plastic material yields (deforms plastically) while a viscoelastic material flows as a liquid

NOMENCLATURE

Symbol	**Description**	**Unit**
C	Concentration	mol/L
F	Force	N
T	Absolute temperature	K
t	Time	s
V_{DPh}	Total volume of emulsion droplets	m^3
V_E	Total volume of emulsion	m^3
ϕ	Dispersed phase volume fraction	%
η	Viscosity	Pa.s/cP
θ	Contact angle	grad
σ	Interfacial tension	N/m

ACRONYMS

AN	Ammonium nitrate
EE	Explosive emulsion
HCEs	Highly concentrated emulsions
IT	Interfacial tension
O/W	Oil-in-water
O/W/O	Oil-in-water-in-oil
PIBSA	Poly(isobutylene succinic) anhydride
SMO	Sorbitan monooleate
Mea	Monoethanolamine, i.e. 2-aminoethanol
W/O	Water-in-oil
W/O/W	Water-in-oil-in-water

CHAPTER 1

Introduction

1.1 BACKGROUND

An emulsion is typically a mixture of two immiscible phases with one dispersed in another. Water-in-oil emulsion type blasting agents were first disclosed by Richard S. Egly, U.S. Pat. No. 3,161,551 (1964). Explosive emulsions are dispersions of water solutions of oxidizers in fuel mediums making them water-in-oil (W/O) type emulsions. The distinguishing characteristic of explosive emulsions, setting them apart from any other typical W/O emulsion, is high oxidizer to fuel ratio – typically starting with 9:1 and reaching as high as 9.6:0.4 – giving these explosive emulsions a unique structure and special characteristics. The need for such a high internal/external phase ratios comes as a result of the necessity for the explosive emulsions to contain close to zero oxygen balance in order to be detonable. Explosive emulsion is the foundation for subsequent products and is termed the *matrix*: it becomes a fully functional industrial explosive *only after* the addition of bulking agent, aluminium or solid ammonium nitrate, as well as high pressure gassing. The main consuming industries for bulk explosives are mining, geological and military. Explosive emulsions based products are highly water resistant, of a particular importance in mining and geological industries (Clay, 1980; ISEE Blasters Handbook, 2010).

The fuel medium typically consists of a mixture of oil and emulsifiers and is termed *continuous* or *external phase* as it surrounds and coats the oxidizer droplets. External phase, due to its relatively lower volume in the emulsion, is spread as a layer thin enough to cover all of the oxidizer. A continuous phase has the greatest influence on the viscosity of the final emulsion (Becher, 1983). Generally, industrially low viscosity oils are used for preparation of continuous phase of pumpable emulsions whereas high viscosity oils are used for production of packaged products. The oxidizer solution dispersed is called *internal* or *discontinuous phase* and exists within the continuous phase in the form of microscopically fine droplets separated from each other in oil. Droplet size also, to a lower extent than external phase, affects the viscosity of final emulsion in the inversely proportional fashion – the lower the droplet size, the higher the viscosity (Becher, 1983). Droplet size is controlled by the amount of input work on the emulsion manufacturing stage in the inversely proportional way – the higher the amount of input work, the lower the droplet size. The internal phase either partially or fully consists of an ammonium nitrate (AN) oxidizer with the addition of inorganic salts such as sodium nitrate and calcium nitrate in cases of partial presence of AN. In addition, a discontinuous phase exists within a continuous in a super cooled state which is dictated by chemical properties of the oxidizer, requiring a set of special procedural conditions for the successful preparation of a water solution (Becher, 1983; Morhard, 1987).

Successive existence of highly concentrated explosive (HCE) emulsions as a system is ensured by the use of emulsifiers (surfactants). Only with the aid of emulsifiers can emulsion remain stabilised against liquid separation, existing, however, in the thermodynamically unstable state with a constant tendency towards destabilisation. Thermodynamic instability of HCE emulsions comes as a result of the above mentioned existence of internal phase in a super cooled state and is related to both coalescence of droplets and phase transition in the form of crystallisation within the dispersed phase (Clay, 1980; ISEE Blasters Handbook, 2010). Overall, thermodynamic instability of those systems may cause partial or full desensitisation of emulsion to detonation (Cooper & Baker, 1989; McKenzie & Lawrence, 1990; Boer, 2003).

To ensure successive formation of HCE emulsions, an emulsifier system must obey certain criteria. Firstly, an emulsifier must contain a certain emulsifying capacity in order to stabilise the system via lowering of interfacial tension on emulsion formation. A second requirement is the ability of an emulsifier to efficiently suppress the coalescence and spreading of crystallisation in internal phase at rest, or, in other words, to provide sufficient shelf-life stability. The final requirement that must be fulfilled is to stabilise and preserve the integrity of the system under high shear conditions. Emulsifier systems currently adopted for industrial use in most cases are meeting a maximum of two of the above mentioned conditions, giving rise to the requirement of a system possessing improved properties that will allow higher stability of explosive emulsions (Richard *et al.,* 2004).

The selection of an emulsifier required to prepare an emulsion explosive is of major importance. Emulsifier directly contributes to the ease of emulsion formation, the discontinuous phase droplet size and the emulsion stability and pumbability (Chattopadhyay, 1996). Emulsifiers that have been used previously were basic hydrophobic surfactants that are able to stabilise W/O emulsion, including oxazolines, salts of long chain fatty acids, sorbitan esters and ethylene oxide condensates of fatty acids (Egly, 1964). As studies progressed, a wide variety of W/O emulsifiers were used, including but not limited to sorbitan fatty acid esters, glycerides of fat-forming fatty acids, polyoxyethylene sorbitol esters, isopropyl esters of lanolin fatty acids and mixtures of higher molecular fatty alcohols and wax esters (Bluhm, 1969). After several years of trials, the choice of major emulsifiers used to stabilise explosive emulsions was narrowed to sorbitan emulsifying agents, in particular, sorbitan fatty acid esters such as sorbitan monolaurate, sorbitan monooleate, sorbitan monopalmitate, sorbitan monostearate and sorbitan tristearate (Wade, 1978). In subsequent years, sorbitan monooleate (SMO) became one of the first surfactants to receive wide industrial recognition, becoming the conventional surfactant used to stabilise explosive emulsions.

It was not until 1995 that Michael Cechanski invented the first emulsifier that could be used on an industrial scale – a polyisobutenyl succinic anhydride (PIBSA) based emulsifier – patented two years later in 1997 (Cechanski, 1997). New PIBSA based emulsifiers had a number of advantages over conventional non-polymeric ones, such as the following:

- increased shelf life stability;
- possibility of developing surfactants able to tolerate higher levels of contaminants within the oxidizer solution; and
- possibility of developing surfactants able to tolerate high levels of waste oils in the fuel phase used to manufacture these emulsion explosives (Chattopadhyay, 1996; Hales *et al.*, 2004).

As a result of these advantages, PIBSA based emulsifiers rapidly substituted the majority of conventional surfactants on the industrial scale production of HCE emulsion explosives and are to date the surfactants of choice for stabilisation of these emulsions. However, in spite of their advantages, all currently used PIBSA based surfactants fail to provide industrially desirable under shear stability, thus restricting transportation and pumping of such emulsions. PIBSA based surfactants also have a high production cost which results in significantly higher cost of emulsions stabilised by these surfactants in comparison to the ones stabilised by SMO.

One of the approaches for solving the issue of when an emulsifier may provide only certain required characteristics of emulsion stabilisation is to create surfactant blends (Binet *et al.*, 1982; Chattopadhyay, 1996; Hales *et al.,* 2004). The addition of non-polymeric emulsifier to the polymeric one provides pumpability of emulsion (Hales *et al.*, 2004). The low molecular weight surfactants are expected to improve under shear stability and flow characteristics, whereas the polymeric surfactants are expected to stabilise emulsions during storage (Yates *et al.*, 1987). This approach makes it possible to suppress coalescence of the supersaturated droplets of the oxidizer salts present in the discontinuous phase and improve stability of the emulsion under high shearing (Cooper *et al.,* 1989). The ratio of polymeric emulsifier to low molecular weight emulsifier is claimed to be 1:25, 3:1, but preferably in the range of 1:5 to 1:1 (Binet *et al.*, 1982; Hales *et al.,* 2004). The ratio of 4:1 for the mixture was used by Chattopadhyay (1996).

1.2 STATEMENT OF THE RESEARCH PROBLEM

Despite all the advantages of the currently used PIBSA/SMO surfactant system, it possesses numerous limitations. For example, PIBSA based surfactants have high production cost, thereby effectively increasing cost of final product. Moreover, another significant problem is higher affinity towards micelle formation than towards binding to W/O interface, generally resulting in using significant amounts of surfactant to stabilise an emulsion.

In blends with PIBSA, SMO destabilises both liquid/liquid interface and micelles which comes as a result of a much higher mobility and much higher solvation factor. Furthermore, SMO causes multilayer crystallisation. All of these factors lead to a significant decrease of shelf life and overall stability of an emulsion.

Very little research has investigated the possibility of the implementation of polyhedral oligomeric silsesquioxane (POSS) nanomolecules as a stabilising system in emulsions, and even less research into highly concentrated emulsions.

1.3 RESEARCH QUESTIONS

The main questions of this current study are as follows:

- Are POSS nanomolecules active within the system of interest?
- Is it possible to form W/O emulsions stabilised with the use of POSS nanomolecules solely?

- If yes, what types of POSS nanomolecules within the scope of this investigation are the most suitable for stabilisation of W/O emulsions?
- Is it possible to form highly concentrated W/O emulsions stabilised with the use of the most suitable POSS nanomolecules solely?
- If not, is it possible to successfully form highly concentrated W/O emulsions stabilised with the use of surfactant system comprising polymeric PIBSA-Mea and most suitable POSS nanomolecules?
- If yes, what is the effect of such a stabilising system and the presence of POSS nanomolecules on the stability of emulsion?
- What are the advantages of implementation of POSS nanomolecules as a co-surfactant within the system of interest?

1.4 OBJECTIVES

The main objectives of this study are to investigate the possibility of incorporation of POSS nanomolecules into the emulsions, the effects of these molecules on the stability of the final system, and the advantages or disadvantages of the use of these molecules within the system of interest.

1.5 DELIMITATIONS OF THE STUDY

The following aspects will *not* be covered in this study:

- gassing and detonation of emulsion;
- effects of dispersed phase concentration on rheological properties and pumpability of highly concentrated explosive emulsions;
- effects of droplet size distribution of the dispersed phase of super concentrated emulsion on rheological properties, ageing and pumpability of highly concentrated explosive emulsions;
- effects of oil polarity on rheological properties and pumpability of highly concentrated explosive emulsions; and
- effects of emulsion formulation content parameters on blasting of explosive emulsion.

This study is subdivided into the following sections:

- **Chapter 1** – serves as an introduction to work.
- **Chapter 2** – covers the necessary fundamentals and provides the background literature relevant to the study.
- **Chapter 3** – provides an overview of the materials and methodology used as part of the experimental stage of the work.
- **Chapter 4** – presents the results obtained by means of experimental work as well as discussions pertaining to these findings.
- **Chapter 5** – offers an overview of the study and results obtained, as well as final conclusions.

1.6 SIGNIFICANCE OF THE RESEARCH

The findings of this study lay crucial ground work with potential benefits for a wide range of industries, from mining, to explosives, to pharmaceutical, to cosmetics and food, all of which use emulsions either as a mode of transportation or a process ingredient for product storage. The main thrust of this study, however, lies particularly with the explosive industries where both long term storage and pipeline pumping are economically viable options.

CHAPTER 2

Theory and Literature Review

2.1 INTRODUCTION

This chapter focuses on the theoretical background of the study. It presents explanations and fundamental concepts of emulsions as a system as well as the high internal phase ratio emulsions. This type of emulsion, the highly concentrated emulsion (HCE), is the system of interest for this current work. The major aspects of stabilisation of such system are discussed, including the review of the currently used stabilising agents with mechanisms of action, and a detailed look at the major mechanisms of destabilisation of the system.

After the introduction of the basic fundamental theory focused on the major aspects of the system, a relatively new approach towards the stabilisation is reviewed: the stabilisation of emulsions by the means of microscopically fine solid particles. Such a system, termed *Pickering emulsion,* leads to the current work focusing on the stabilisation of HCEs with the nanomolecules. A theoretical background of the POSS nanomolecules is presented, including such aspects as structure and type of compound, as well as the fields in which these compounds are implemented most frequently.

The major concepts covered in this chapter include but are not limited to the following:

- general definition of emulsion;
- highly concentrated emulsion;
- general consideration of emulsion stability;
- factors determining emulsion stability;
- major surfactants and their mechanism of action;
- Pickering emulsions;
- structural overview of POSS nanomolecules; and
- general implementation of POSS nanomolecules.

2.2 EMULSIONS: GENERAL OVERVIEW

An *emulsion* is a system comprising two immiscible liquids, one uniformly dispersed within another in the form of fine microscopic droplets. The two phases of emulsion are generally aqueous and oil, in both cases individually containing other components within them. These phases are termed *dispersed phase* and *continuous phase* depending on the type of emulsion, or in other words, on which phase exists in the form of dispersed droplets within another. General two phase emulsions are termed *simple emulsions.* Two basic types of simple emulsions exist, as illustrated in Figure 2.1 (McClements, 2005):

- *Oil-in-water* (O/W) emulsion, with oil being a dispersed phase in the continuous aqueous phase;
- *Water-in-oil* (W/O) emulsion, with aqueous solution existing as a disperse within the oil phase.

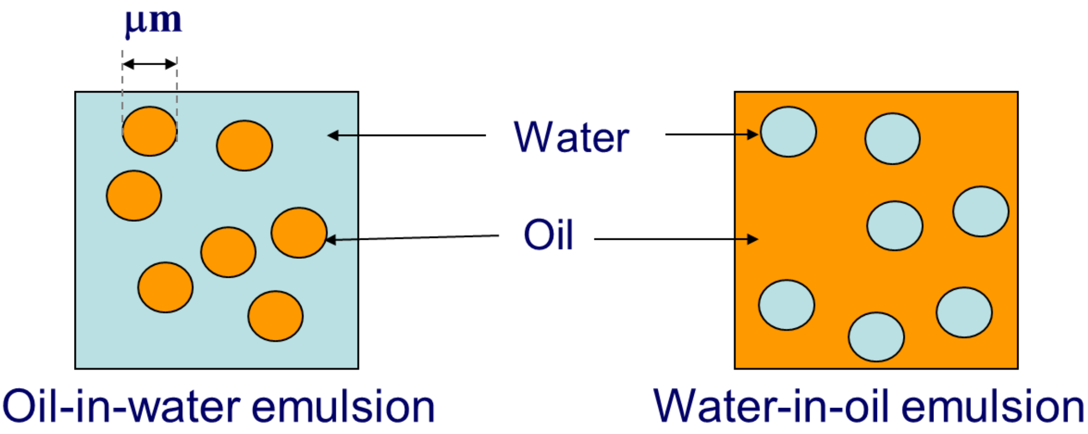


Figure 2.1: Schematic illustration of O/W and W/O type emulsion system

Additionally, a more complex system exists, namely water-in-oil-in-water (W/O/W) or oil-in-water-in-oil (O/W/O) which is termed *multiple emulsions*. As follows from the name, these are conceptually the same type of system with the exception of the dispersed phase being itself a dispersion of two liquids. These systems are less common than general simple type emulsions and fall outside the scope of this present study; therefore, no in depth overview is presented within the framework of this study. A comparison of the general structures of various types of simple and multiple emulsions are presented in Figure 2.2 (Bouyer *et al.*, 2012).

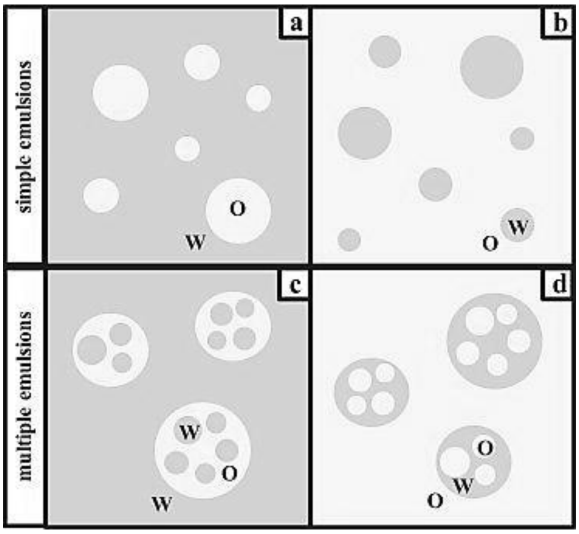


Figure 2.2: Schematic comparison of various types of emulsions: a) O/W, b) W/O, c) W/O/W, d) O/W/O (Bouyer *et al.*, 2012)

Emulsions, be they simple or multiple, are further classified into *concentrated* and *dilute* on the basis of the dispersed phase concentration within the continuous phase (McClements, 2005). Figure 2.3 illustrates schematic comparison of the two classes of the system.

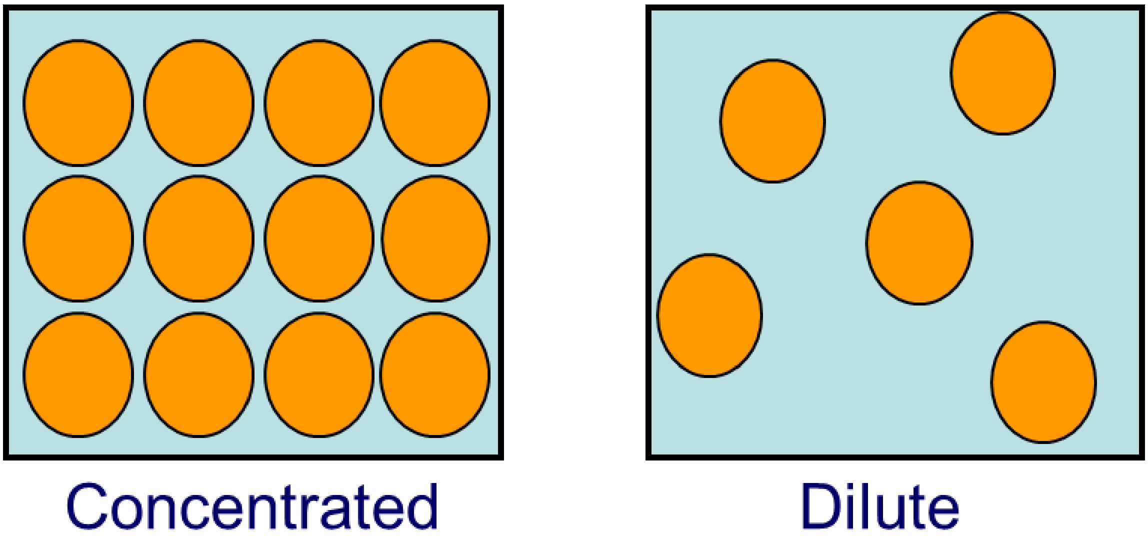


Figure 2.3: Schematic illustration of concentrated and dilute emulsion

Dispersed phase concentration of emulsion is characterised by means of dispersed phase volume fraction (ϕ), calculated using Equation 2.1 as follows (McClements, 2005):

$$\phi = \frac{V_{Dph}}{V_E}$$

Equation 2.1

Where:
V_{DPh} is the volume of dispersed phase and V_E is the total volume of the emulsion.

Emulsion is classified as concentrated, or highly concentrated, if the dispersed phase concentration within the system is above 74%. In highly concentrated emulsions (HCE), individual droplets are unable to maintain a perfect spherical shape due to the high packing factor which leads to deformation and results in a closely-packed hexagonal configuration (Figure 2.4). Furthermore, this causes these droplets to be in constant contact with each other as well as restricted in mobility, as compared to the dilute system (Webber & Engineers, 1999).

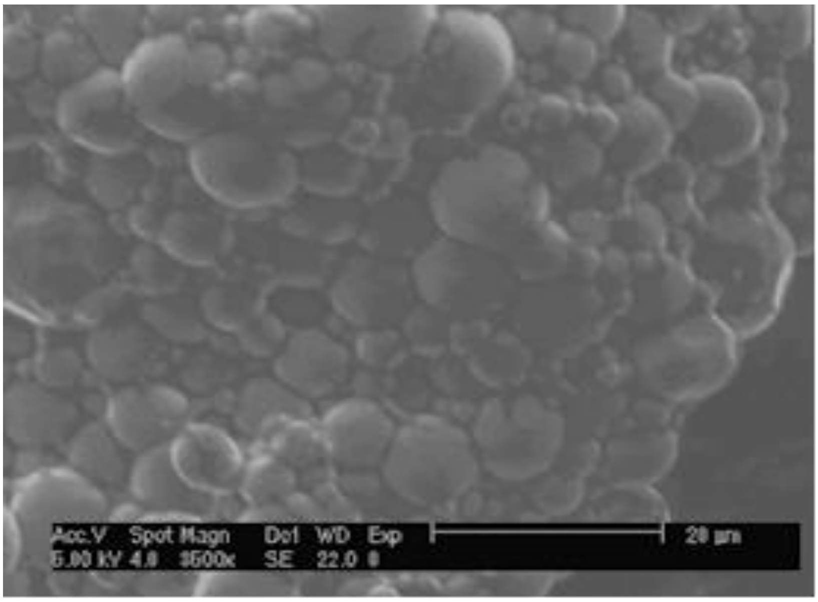


Figure 2.4: Microscopic image of an HCE illustrating droplet deformation due to high packing factor (taken in the Rheology Laboratories at the Cape Peninsula University of Technology)

The volume fraction in these systems can reach as high as 99% and stabiliser concentration as low as 0.5% by weight; the final emulsion takes a gel-like structure (Aronson & Petko, 1993; Binks, 1998; Kizling *et al.*, 2006).

2.3 EXPLOSIVE GRADE HIGHLY CONCENTRATED EMULSIONS

Current work is focused on a class of highly concentrated W/O emulsions used as a matrix for industrial explosives within the mining sector of industry. These are typically liquid pumpable industrial explosives delivered to the site of detonation through a system of pipes. The main fields of use for these compounds include, but are not limited to, coal mining, metal and non-metal mining, construction and quarrying. The advantages offered by such types of explosives over other industrial explosives such as dynamite are increased safety, ease of delivery and implementation in a complex environments, as well as storage advantages and higher cost effectiveness (Clay, 1978; Sudweeks & Jessop, 1980).

Much research and numerous systematic studies have been conducted over the past decade relating to highly concentrated explosive emulsions, with a significant number of published works covering all aspects of those systems (Gaicha *et al.,* 1995; Chattopadhyay, 1996; Malkin *et al.*, 2004; Malkin & Masalova, 2007; Masalova, 2003; Masalova & Malkin, 2007a; 2007b; 2007c; 2008; 2013; Masalova *et al.,* 2003; 2005; 2006, 2011a, 2011b; Hales *et al.,* 2004; Reynolds *et al.,* 2000; 2001; 2002; 2009; 2011; Thsilumbu *et al.,* 2010; Yaron *et al.,* 2011). The majority of research and work in this field has been conducted and covered by Masalova *et al.* (2003-2013) and White *et al.* (White *et al.,* 2004; Reynolds *et al.,* 2000; 2001; 2002; 2009; 2011) with both groups of researchers complementing each other's work. Masalova *et al.* investigated a variety of aspects relating to HCE emulsions (e.g. rheological properties, manufacturing process and storage properties) and White *et al.* provides a better insight into the mechanisms occurring within the system by the means of small angle neutron scattering.

As was mentioned in the introduction to the study, these types of blasting agents were first introduced by Richard S. Egly in 1994. Typically such a system is a dispersion of an oxidizer solution within an oil media with a dispersed phase ratio starting at 90% by weight of emulsion and reaching, when necessary, up to 96%. The matrix itself on the stage of preparation is non-detonable and is required to undergo additional manufacturing stages to become a fully functional industrial explosive (Clay, 1980; ISEE Blasters Handbook, 2010). Oxidizer dispersion of the system is either fully or majorly consists of a super saturated solution of ammonium nitrate (AN) which enhances the product's cost effectiveness. Depending on the formulations of various individual products other possible components of the aqueous phase of emulsion may include but are not limited by sodium nitrate and calcium nitrate (Becher, 1983; Morhard, 1987). The continuous phase of the system comprises industrial grade oils typically of a low viscosity to allow pumpability, and added surfactant. The choice of stabilising agents, or emulsifiers, plays a critical role in formulation and manufacturing of HCE explosives. These compounds ensure the general existence of the system as they strongly affect emulsion formation, the discontinuous phase droplet size and overall emulsion stabilisation and ability for transportation to the site of detonation (Chattopadhyay, 1996; Clay, 1980; ISEE Blasters Handbook, 2010).

2.3.1 Instability aspects of HCE explosives

The highly concentrated emulsion matrix under discussion for this current study is a system with a constant tendency towards destabilisation as a result of various factors. The supersaturated dispersed phase, with a typical inorganic salt concentration of 80% and above, exists in a super cooled state within the system at ambient temperatures. This leads to a thermodynamic instability of the system related to crystallisation within the dispersed phase (Clay, 1980; ISEE Blasters Handbook, 2010). Such a crystallisation, when reaching a substantial level, results in a desensitisation of the explosive to detonation as well as affects the pumpability (Coolbaugh & Mahamat, 2003). A number of studies identified various factors affecting the crystallisation of emulsions dispersed phase:

- the oil type, and hence properties, used as part of the continuous phase of the system;
- surfactant type, properties and mode of action dictating its behaviour at the phase interface (Ganguly *et al.,* 1992; Ghaicha *et al.,* 1995; Maheshwari & Dhathathreyan, 2004);
- concentration of the oxidizer within the aqueous phase (Ganguly *et al.,* 1992);
- concentration of dispersed phase in the system (Kharatiyan, 2005; Masalova *et al.,* 2006); and
- general contaminations and impurities such as dust and ions (Becher, 1983; Adya & Neilson, 1991).

Crystallisation of dispersed phase may occur both from within the droplets – with growth progressing towards the interface of the two phases (Becher, 1983; Adya & Neilson, 1991) – as well as at the surface of the droplet with progression into the interior (Somasundaran, 2006; Tshilumbu *et al.,* 2010). After crystallisation is initiated, it has the potential of spreading throughout the bulk structure of emulsion (Becher, 1983; Kharatiyan, 2005; Masalova *et al.*, 2006). Both the commencement time of crystallisation and the spreading rate depend on the stability and rigidity of the droplet interface as well as the inter-droplet layer (White *et al.,* 2004; Kharatiyan, 2005).

Additional outcomes of system instability include creaming, sedimentation, flocculation, coalescence and the phase separation, as shown in Figure 2.5 (Binks, 1998). *Creaming* is a phenomena occurring in O/W emulsion as a result of gravitational influence on the droplets of dispersed phase, which, in the case of such a system, are of lower density than the continuous aqueous phase. In general, creaming of O/W emulsion is an easily reversible process by means of gentle agitation of the system. In a W/O system, due to the dispersed phase being of higher density, an equivalent process is sedimentation (Binks, 1998; McClements, 2005).

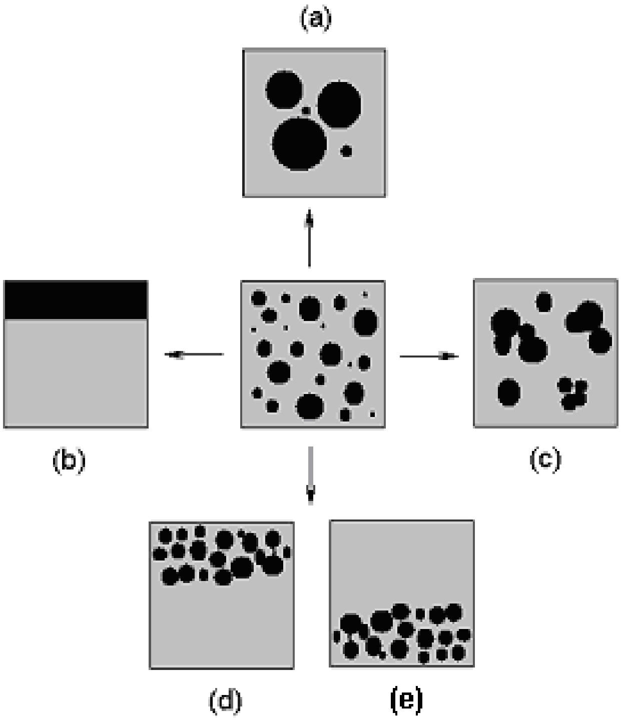


Figure 2.5: Emulsion structure degradation as a result of destabilisation: a) coalescence; b) phase separation; c) flocculation; d) creaming; e) sedimentation (Myers, 1992)

Flocculation is the phenomena of aggregation of individual droplets of dispersed phase without structural change. Due to the critical concentrations of the dispersed phase within the system under investigation, as discussed previously, such a phenomenon is impossible to occur in such a system. However, this may be a considerable factor in the low concentrated emulsion. This can be both easily reversible as well as hardly or non-reversible (Binks, 1998).

As opposed to flocculation, *coalescence* is the process in which two or more individual dispersed phase droplets fuse together resulting in the formation of a single large size drop. This is an irreversible change of structure. Contrary to flocculation, this phenomenon is more uncommon in the dilute emulsions but is one of the main destabilisation outcomes within the highly concentrated systems as a result of a close packing of individual droplets within the structure (Binks, 1998). Extensive and aggressive coalescence eventually leads to a complete phase separation, or in other words, a full degradation of internal structure of highly concentrated emulsion (McClements, 2005). Consequently, besides of the crystallisation of the dispersed phase of the system, the only other main type of destabilisation of the system of interest is coalescence of individual droplets. Therefore, other types of destabilisation mentioned will not be considered as part of this current study.

2.4 EMULSIFYING AGENTS

A brief history of emulsifiers was presented in Chapter 1. This section focuses on the overview of currently adopted liquid emulsifiers, or surfactants, with consideration of the general structure and properties of these compounds as well as the mode of action in the system, and advantages and disadvantages of each when used individually. In addition, an overview of a widely implemented surfactant blend will be presented.

2.4.1 Sorbitan Monooleate (SMO)

Sorbitan Monooleate (SMO) is a non-polymeric anionic surfactant and, as an emulsifier, it meets a range of criteria required for stabilisation of W/O HCE emulsions, but most importantly, its low HLB of about 4.3 gives it a high affinity towards oil (Ghaicha *et al.,* 1995). Its low molecular weight of 428 is also a big advantage, making sorbitan monooleate a highly mobile molecule (Yaron *et al.,* 2011). SMO is comprised of an 18-carbon oleic acid hydrophobic tail and a hydrophilic sorbitan head: Figure 2.6 illustrates the SMO molecular structure. Due to its high mobility and high affinity towards oil, SMO provides high under shear stability, allowing for industrial transportation and numerous pumping cycles. Surfactant molecules rapidly rush onto the W/O interface and bind to it strongly due to a high solvation energy of -600 kj/mol (Yaron *et al.,* 2011).

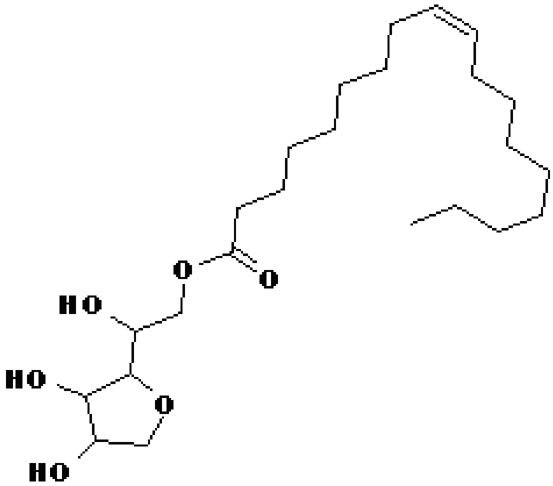


Figure 2.6: General molecular structure of SMO

An added advantage of SMO is its low production cost, of critical importance on industrial scales. While SMO provides a very high under shear stability, on the other hand, it unfortunately does not provide desirable long term shelf life stability (Hales *et al.*, 2004; Gaicha *et al.,* 1995; Tshilumbu *et al.,* 2010). Various attempts to improve the storage characteristics of emulsion explosive compositions have still concentrated on the emulsifier component of the compositions, particularly on the selection of suitable emulsifier, or blends thereof, which are designed to suppress coalescence of the supersaturated droplets of the oxidizer salts present in the discontinuous phase (Cooper & Baker, 1989). The commercial trade name of sorbitan monooleate emulsifying agents is Span®80. Figure 2.7 presents one of the possible conformations of an SMO molecule.

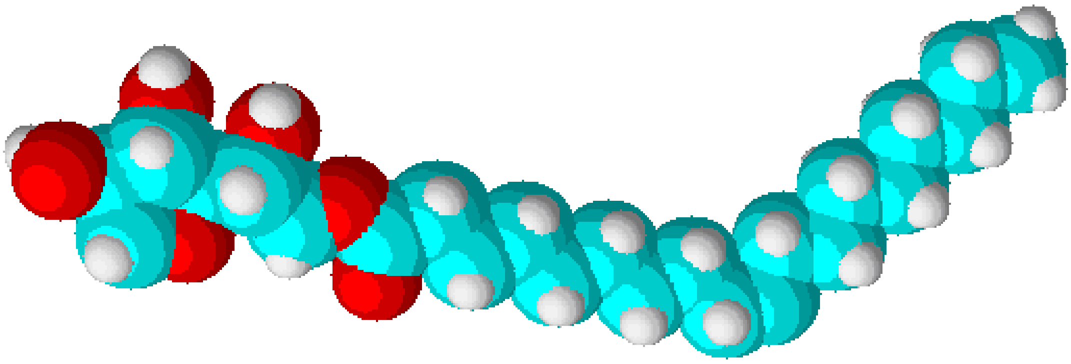


Figure 2.7: 3-D representation of the possible conformation of SMO molecule (with oxygen atoms presented in red, carbon in light blue and hydrogen in white)

2.4.2 Polyisobutenyl Succinic Anhydride (PIBSA) based surfactants

PIBSA based surfactants are oligomeric, as opposed to the monomeric SMO molecules, with low HLB (<4) compounds with molecular weight above 1000, a long hydrophobic carbon tail and a hydrophilic polar head. The polarity of a head group can significantly influence adsorption of emulsifier molecules at the interface: an increase in polarity demonstrates increased adsorption and if the polarity is decreased, the adsorption of surfactant is reduced (Papke & Robinson, 1994; Masalova *et al.,* 2011). The type of PIBSA based surfactant used in this study is PIBSA-Mea with the head group of this molecule presented in Figure 2.8.

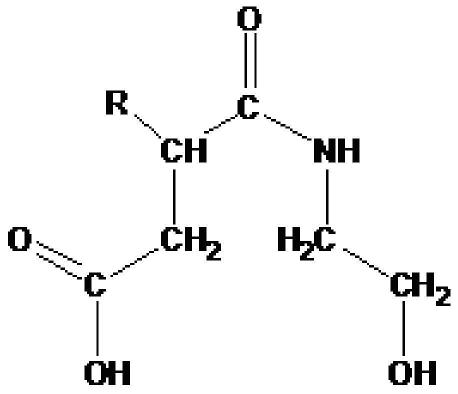


Figure 2.8: Head group structure of PIBSA-Mea molecule

PIBSA based surfactants are usually produced by two steps: 1) the synthesis of PIBSA and 2) the addition of alkanol amine derivatives. Most commonly used in the production of olefin is polyisobutylene. One of the reasons for its preference is its extensive branching, allowing the derived emulsifier to possess excellent oil solubility in both the non-associated and associated forms (Rudnick, 2003). With a long chain tail, these surfactants offer a significant increase in shelf life stability in comparison with low molecular weight surfactants. On the other hand, high molecular weight from presence of a long tail decreases the mobility of the molecules resulting in weaker binding at the aqueous-oil interface. Another factor contributing to a weaker interfacial stabilisation is low solvation energy of about -100 kj/mol, much lower than that of SMO. An oligomeric tail of PIBSA based molecules under discussion consists of a chain of 19 units of the structure $-C(CH_3)_2-CH_2-$ linked to one another resulting in, when contained in a single chain, a total length of 38 carbon atoms. An additional 38 carbon atoms are contained within the methyl side groups bonded to the main chain. One of the possible conformations of a PIBSA-Mea surfactant molecule is illustrated in Figure 2.9. Additionally, as opposed to SMO, PIBSA based surfactants have substantially higher production costs, effectively increasing the cost of any products in which they are implemented.

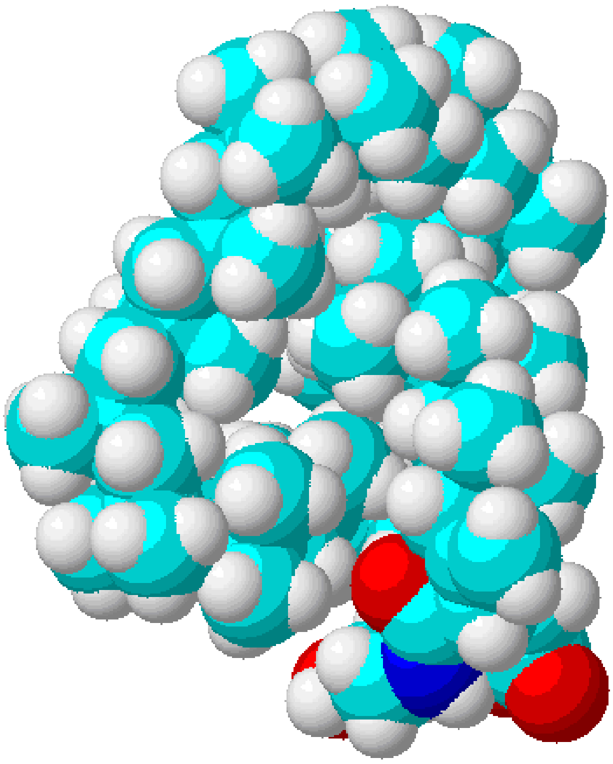


Figure 2.9: 3-D representation of the possible conformation of PIBSA-Mea molecule (with oxygen atoms presented in red, nitrogen in dark blue, carbon in light blue and hydrogen in white)

2.4.3 PIBSA-Mea/SMO emulsifying system

The most widely industrially used emulsifier blend targeted for improvement of under shear stability of explosive emulsions stabilised by PIBSA based surfactants is with conventional SMO. Emulsions stabilised by the above described blend of emulsifiers result in a compromise, with moderate shelf life and under shear stability characteristics (Hales *et al.,* 2004; Gaicha *et al.,* 1995; Masalova *et al.,* 2011a).

It has been shown by Masalova *et al.* (2011a), via the study of crystallisation mechanism, that crystallisation process in HCE emulsions does not take place within the boundaries of individual droplets but rather occurs by breaking through droplet boundaries and the growth of crystalline structures in several droplets simultaneously. This suggests a much higher importance of surfactants' nature for the overall stability of HCE emulsions (Masalova *et al.,* 2011a). The same study has shown that the time to crystallisation occurrence for the emulsions stabilised with PIBSA-Amide/SMO surfactant system is reduced significantly in comparison with PIBSA stabilised emulsions (3700 hours vs 5040 hours), but at the same time, increased significantly in comparison to SMO stabilised emulsions (3700 hours vs 840 hours).

While PIBSA/SMO surfactant blends have advantages in stabilisation of HCE emulsions, there is also a range of problems associated with those blends and resultant emulsions. Systematic research conducted by Masalova *et al.* and White *et al.* throughout a number of years has revealed a number of disadvantages associated with those blends (originated from PIBSA properties and SMO properties, as well as the effects in the mixture of both) and resultant emulsions. PIBSA based surfactants, as mentioned previously, have high production costs that affect the cost of the end product. Those surfactants form only a single layer around the droplet with stability reached via the interaction of surfactant molecule head groups with AN and through the interaction of entanglements between PIBSA tails (Reynolds *et al.,* 2000). The issue lays with a high tendency of PIBSA based surfactants towards the formation of spherical reverse micelles in the continuous phase with stability reached by the means of a steric barrier (Reynolds *et al.,* 2000; 2001; 2009), as illustrated by Figure 2.10.

PIBSA based surfactants have a higher affinity towards reverse micelles formation than reaching the aqueous-oil interface resulting in high concentrations to be required for stabilising the emulsion (Reynolds *et al.,* 2000; 2001; 2009). Out of the total amount of emulsifier in the system, only 12%-16% reaches the interface while the rest forms reverse micelles (Reynolds *et al.,* 2000). This in turn leads to the additional issue of potential destabilisation of the system by inverse micelles as soon as micelle fraction reaches a critically low value that may be higher than the critical micelle concentration (CMC) (Masalova *et al.,* 2011a).

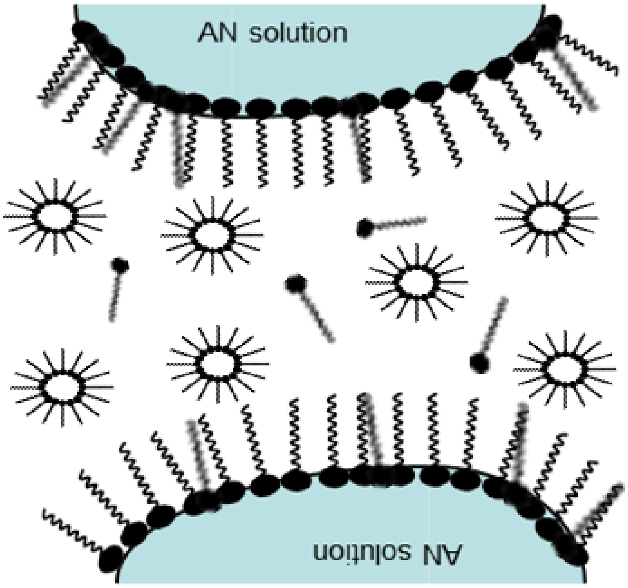


Figure 2.10: Schematic illustration of the mechanism of emulsion stabilisation by means of PIBSA-Mea surfactant

While addition of SMO as a co-surfactant does increase under shear stability, at the same time, it further destabilises the system and reduces shelf life stability (Gaicha *et al.,* 1995; Hales *et al.,* 2004; Masalova *et al.,* 2011a; Tshilumbu, 2010). Sorbitan monooleate is a much smaller and a much more mobile surfactant than any PIBSA based emulsifier. This results in SMO molecules reaching and occupying the phase interface much faster during the emulsification process (Yaron *et al.,* 2011). As opposed to polyisobutenyl succinic anhydride based emulsifiers, the molecules of sorbitan monooleate have a high tendency towards formation of molecular multilayer at the phase interface. Such a structure becomes gradually opaque with time, effectively inducing crystallisation at the interface (Opawale & Burgess, 1998; Drelich *et al.*, 2010). A schematic illustration of this phenomenon is presented in Figure 2.11.

After SMO molecules occupy the interface, they are hardly and only partially replaced by PIBSA molecules (Masalova *et al.*, 2011b) for reasons of both solvation energy being six times higher in SMO than in PIBSA and a high tendency of SMO molecules towards the formation of multiple hydrogen bonds with AN molecules (Masalova *et al.*, 2011b). This results in a significant decrease of shelf life stability of the emulsion due to the presence of a much lower number of PIBSA molecules at the phase interface. Another destabilising effect that arises in the system with the addition of SMO as a co-surfactant is related to reduction in stability of micelles as a result of SMO molecule insertion into PIBSA-Mea micelles with subsequent compromising of the structure and strength of tail interactions due to incompatibility of the SMO tail chain length with that of PIBSA-Mea (Gaicha *et al.*, 1995; Reynolds *et al.*, 2009; Yaron *et al.*, 2011). It has been demonstrated that the use of parafin oil compensates the incompatibility of chain length, thereby suppressing the micelle destabilisation to a certain degree (Chattopadhyay, 1996).

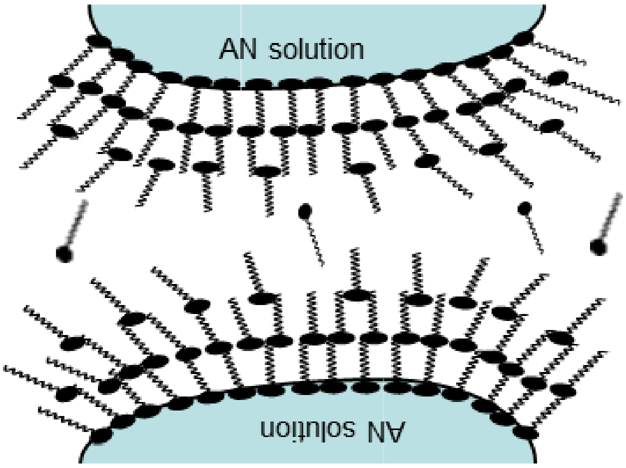


Figure 2.11: Schematic illustration of the multilayer formation by the SMO molecules

Research conducted by Kovalchuk (2009) has shown that synergy in the PIBSA/SMO mixtures, both at the aqueous-oil interface and in micelles, is only observed at significantly low SMO concentrations. The addition of as little as 9% SMO to the oil phase results in 50% interface coverage.

The study of rheological properties of PIBSA/SMO stabilised HCE emulsions conducted by Masalova *et al.* (2011a) has demonstrated the following results:

- both interfacial tension and interfacial dilational elastisity (elastic modulus) of emulsion stabilised by PIBSA-Amide/SMO (10:1) surfactant blend showed a significant decrease in comparison to the PIBSA-Amide stabilised system and a significant increase in comparison to SMO stabilised system;

- visco-elastic behaviour of the system; and

- addition of low molecular weight surfactant to the formulation significantly decreases the resistance against flow at intermediate to high shear rate regime with yield stress values of PIBSA/SMO system being lower than systems stabilised solely by any PIBSA based surfactant.

2.5 EMULSION STABILISATION WITH SOLID PARTICLES

Different approaches to emulsion stabilisation and the concept of emulsifier have attracted increasing interest in recent years. Besides the commonly used amphiphilic molecules, emulsifiers can be nanometer-sized solid particles that adsorb at the liquid-liquid interface and form a protective film between the dispersed phase and the continuous phase (Dutschk *et al.*, 2007; Chen *et al.*, 2011). Pickering (1907) has reported water/paraffin emulsion stabilised by basic copper and iron sulphate solid colloidal particles; such emulsions have been termed *Pickering emulsions*. Pickering emulsions stabilised solely by nanoparticles attract more interest in recent years of various industries such as explosives, pharmaceutical and cosmetics for having high stabilisation and unusual rheological properties (Abend *et al.*, 1998; Binks, 1998; Midmore, 1998; Lagaly *et al.*, 1999; Ashby & Binks, 2000; Binks & Lumsdon, 2000; Melle *et al.*, 2005; Simovic & Prestige, 2007; Kim *et al.*, 2008; Akartuna *et al.*, 2008; Madivala *et al.*, 2009; Morishita *et al.*, 2009; Dickinson, 2010). A wide variety of solid particles, including organic particles (such as polymer latex and polymer micelle) and inorganic particles (such as silica, hydroxides, ferric oxide, titanium dioxide, carbon, and clay particles), have been used for the stabilisation of emulsions (Binks & Lumsdon, 2000; Binks, 2002; Binks *et al.*, 2007a; 2007b).

2.5.1 Stabilisation and properties

Stabilisation of Pickering emulsions is subject to numerous conditions that may be summarised as follows (Levine & Sanford, 1985; Aveyard *et al.*, 2003; Fournier *et al.*, 2009; Varka *et al.*, 2010):

- particles in use must be small enough to exist in the inter droplet layer of emulsion;
- weak flocculation of the particles should occur; and
- partial wetting of the particles by both phases must occur.

The last condition is pointing to the contact angle (θ) being in the range of 0^o to 180^o. Generally it has been observed that hydrophobic particles with a contact angle lower than 90^o have a tendency towards the formation of O/W emulsions, whereas hydrophilic ones with a contact angle higher than 90^o tend towards the formation of W/O emulsions (Binks, 2002), as illustrated in Figure 2.12. Despite this general theoretical range of contact angle, it has been estimated that particles with contact angles in the specific narrow range have a higher probability of stabilising an emulsion than those out of these ranges. The optimal estimated ranges are as follows: 70° to 86° for O/W emulsion stabilisation and 94° to 110° for W/O emulsion stabilisation (Binks, 2002). It is important to point out that an aggregation of particles leads to the formation of a three-dimensional network within the continuous phase, thus effectively blocking the oxidizer droplets and resulting in additional stabilisation of the system (Binks, 2002; Arditty *et al.* 2005).

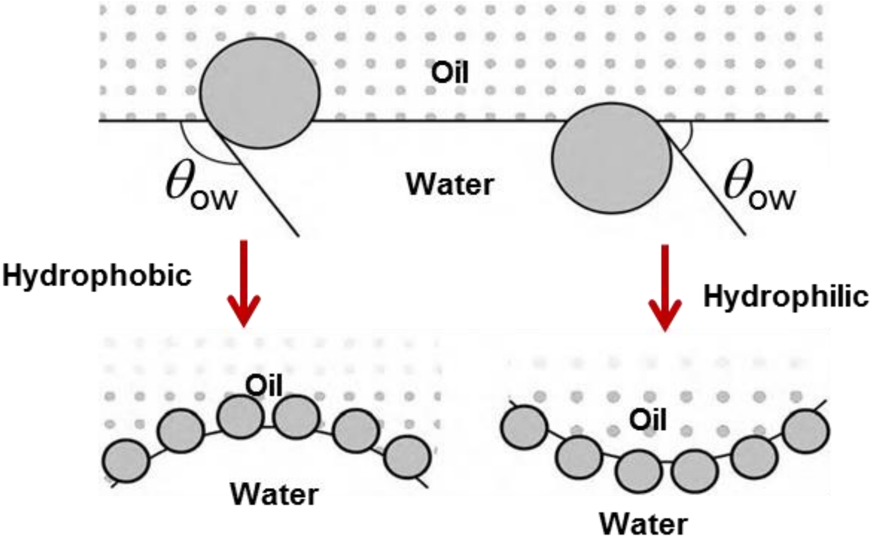


Figure 2.12: Schematic illustration of the influence of contact angle on the type of emulsion formed (Binks, 2002)

2.5.2 Manufacturing of highly concentrated Pickering emulsions

Manufacturing of stable Pickering emulsions has been successfully established by various cosmetic and food industries. Examples of products based on Pickering emulsions currently in use include sunscreens stabilised by solid particles, ice creams stabilised by ice crystals, and whipped creams stabilised by fat particles. All of these products and manufacturing processes are producing Pickering emulsions with low internal phase concentrations. Stabilisation of emulsions containing discontinuous phase concentrations higher than 70% solely by microscopic solid particles becomes extensively difficult. Studies and trials have shown a general tendency for phase inversion phenomenon of emulsion transformation from W/O type to O/W and vice versa in emulsions stabilised exclusively by nanoparticles with a dispersed phase concentration from 65 to 70% (Binks & Lumsdon, 2000).

A presently adopted solution to above mentioned problem is the creation of emulsion formulations containing both classical surfactants and nanoparticles as an emulsifying system. While a number of studies and trials have been conducted recently, the influence of particles in combination with surfactants on the stabilisation of fluid interfaces remains poorly understood (Whitby *et al.*, 2009). Moreover, there have been very few systematic studies conducted that consider the manufacturing of highly concentrated W/O emulsions.

The basic idea behind the addition of surfactants with nanoparticles is to alter the wettability of the particles in order to promote particle adsorption at the interface. During this process, surfactant molecules are adsorbed onto the surface of solid particles, with the resultant combination illustrated schematically in Figure 2.13 by the example of surfactant molecules being adsorbed on the surface of silica nanoparticles (Midmore, 1998; Binks *et al.*, 2007; Drelich *et al.*, 2010).

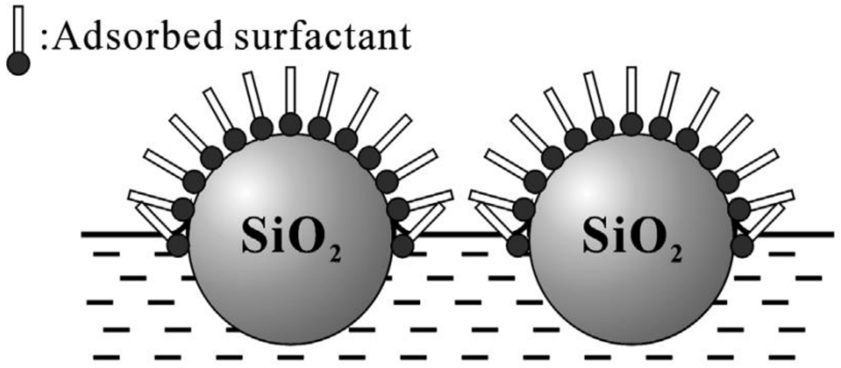


Figure 2.13: Schematic illustration of the influence of contact angle on the type of emulsion formed (Binks *et al.*, 2007b)

The addition of surfactants may also be a tool for altering such properties as flow behaviour, stability, and to some degree, the structure of Pickering emulsions (Velev *et al.*, 1996; Havre & Sjoblom, 2003; Gonzenback *et al.*, 2006; Lagaly *et al.*, 1999). Various interesting experimental trials have been conducted with numerous surfactants of different types in an attempt to reach that goal (Midmore, 1998; Binks *et al.*, 2007). Reports of the listed studies, however, focused on O/W type emulsions. Among the most successful and promising types of nanoparticles are fumed silica nanoparticles. Midmore (1998) has shown various interesting properties on manufacturing of the emulsification system between colloidal silica particles with non-ionic surfactant: a high degree of synergism was observed between silica particles and surfactant molecules. The same study also showed an increase in hydrophobicity of the original hydrophilic particles with the addition of certain surfactants that in turn resulted in an increase of overall stability of emulsion (Midmore, 1998).

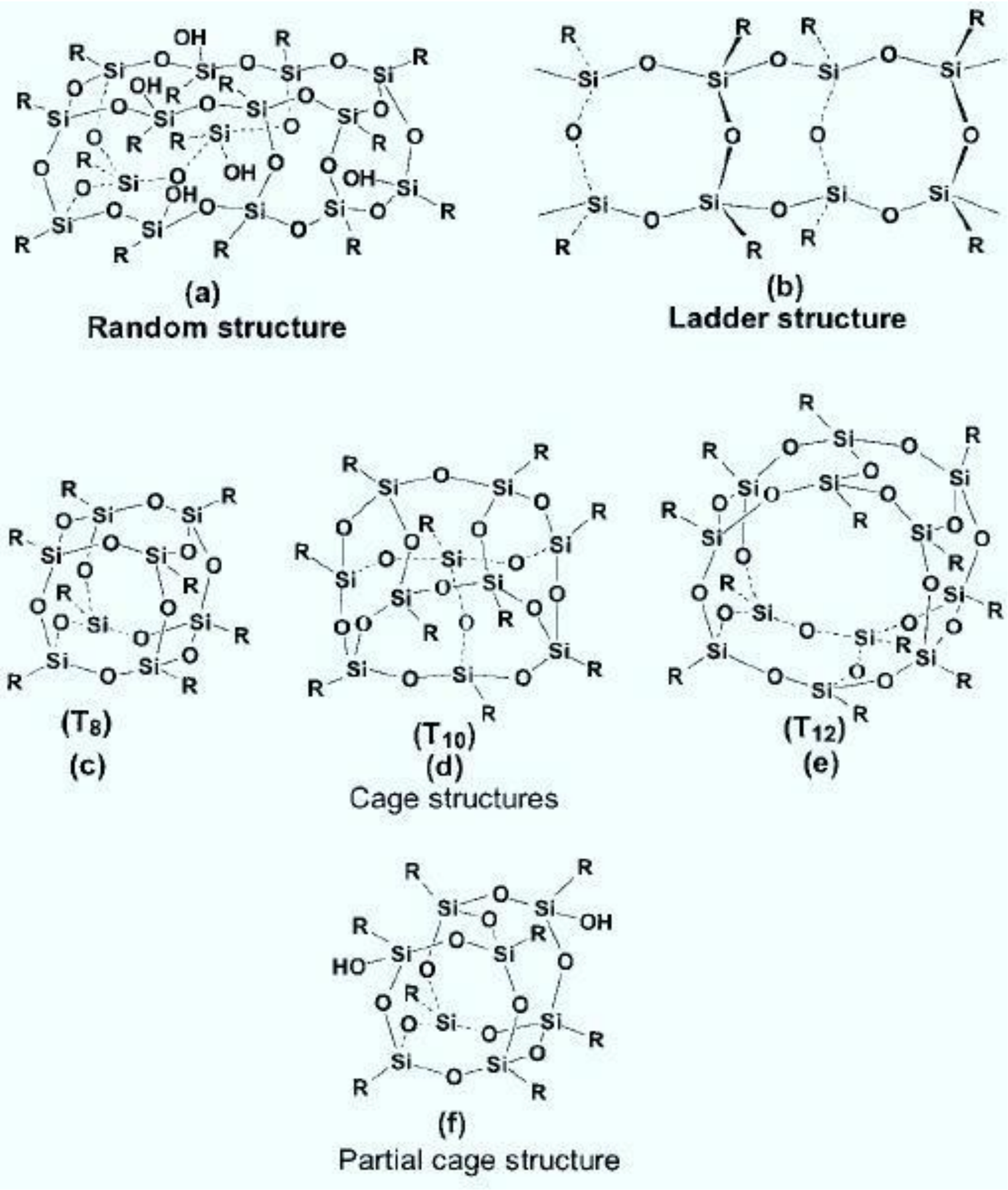
2.6 EMULSION STABILISATION WITH NANOMOLECULES

2.6.1 Structure and properties

The term *silsesquioxane* refers to all structures with the empirical formula $RSiO_{1.5}$, where R is hydrogen or any alkyl, alkylene, aryl, arylene, or organofunctional derivative of alkyl, alkylene, aryl, or arylene groups. The silsesquioxanes include random structures, ladder structures, cage structures, and partial cage structures, as shown in Figure 2.14 (Baney *et al.*, 1995).

The first oligomeric organosilsesquioxanes, $(CH_3SiO_{1.5})n$, were isolated by Scott in 1946 along with other volatile compounds through thermolysis of the polymeric products obtained from methyltrichlorosilane and dimethylchlorosilane cohydrolysis (Scott, 1946). In recent years, much more attention has been afforded to the silsesquioxanes with specific cage structures. These polyhedral oligomeric silsesquioxanes, designated by the abbreviation POSS, are a unique class of compounds. They possess a hybrid inorganic–organic architecture with inner inorganic framework of silicone and oxygen with general formula $(SiO_{1.5})x$ that is externally covered by organic substituents. Covering substituents may be both hydrocarbon in nature or embody a range of polar structures and functional groups (Guizhi *et al.*, 2001). Figure 2.15 illustrates the general structure of a POSS compound.

POSS nanostructured chemicals, from 1 to 3 nm in diameter, can be considered the smallest possible particles of silica or molecular silica. The presence of organic substituents on its outer surface distinguishes these compounds from silica, silicones, or fillers and makes the POSS nanostructure compatible with polymers, biological systems or surfaces.



(a) Random structure

(b) Ladder structure

(T_8) (c)

(T_{10}) (d)

(T_{12}) (e)

Cage structures

(f) Partial cage structure

Figure 2.14: Illustration of the various types of silsesquioxane molecular structure (Baney *et al.*, 1995)

The existence of the potential towards manipulation of the organic component of the molecules opens a wide range of possibilities in the design of the molecules, specifically for the particular systems of interest. Another advantage of the POSS compounds is that unlike large numbers of traditional organic compounds, they release no volatile organic components, rendering them odourless and environmentally friendly (Guizhi *et al.*, 2001).

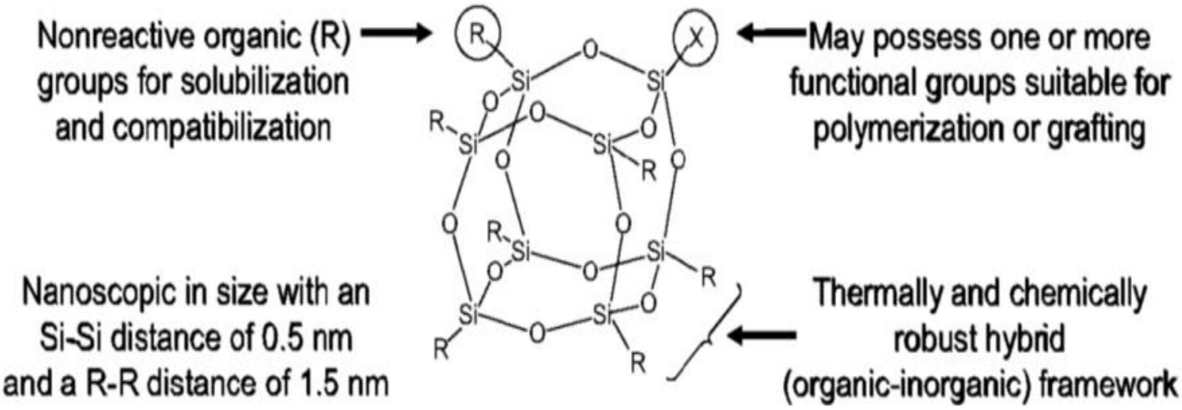


Figure 2.15: General structure of a POSS compound (Guizhi *et al.*, 2001)

A variety of POSS nanostructured chemicals which contain one or more covalently bonded reactive functionalities that are suitable for polymerization, grafting, surface bonding or other transformations, have been prepared (Lichtenhan *et al.*, 1999; 2001).

2.6.2 Applications

A selection of POSS chemicals now exist that contain various combinations of non-reactive substituents and/or reactive functionalities. POSS nanostructured chemicals may, therefore, be easily incorporated into common systems such as plastics via copolymerization, grafting, or blending (Haddad *et al.*, 1999). POSS compounds have been successfully incorporated in the field of polymer research and production, allowing the manipulation of such properties as maximum use temperature, oxidation resistance, surface hardening, and improved mechanical properties, as well as reductions in flammability, heat evolution and viscosity during processing. These enhancements have been shown to apply to a wide range of thermoplastics and a few thermoset systems (Ellsworth & Gin, 1999; Haddad *et al.*, 1999). It is especially convenient that the use of POSS monomers does not require dramatic changes in processing, as monomers are simply mixed and copolymerized. As long as the POSS monomer is soluble in the monomer mixture, it is incorporated in a true molecular dispersion into the copolymer. No phase separation will occur although some aggregation of POSS units bound with the polymer may occur (Guizhi *et al.*, 2001).

There are a variety of applications of POSS molecules beyond polymeric materials. POSS nanostructures have demonstrated significant promise for use in catalyst supports and biomedical applications as scaffolds for drug delivery, imaging reagents and combinatorial drug development (Guizhi *et al.*, 2001). The use of a phosphine-substituted POSS as a core for building new types of dendritic macromolecules has been reported (Hong *et al.* 1997). Incompletely condensed POSS cages have been used to synthesise metal-containing, closed-cage polyhedral silsesquioxanes for use as silica supported metal catalysts (Murugavel *et al.*, 1996; Feher *et al.*, 1997; Ukrainczyk *et al.*, 1997; Duchateau *et al.*, 1998a; 1998b; 1999; Annand *et al.*, 1999; Edelmann *et al.*, 1999; Lorenz *et al.*, 2000).

2.6.3 Implementation in emulsions

Scarcely any research has been conducted investigating the possibility of implementation of POSS molecules in emulsions, and even less concerning highly concentrated emulsions. Recently polihedral oligomeric silsesquioxanes found application in development of latent electrostatic images via the addition of POSS molecules to the toner composition. Preparation of toner particles involves POSS molecules with chemically bonded resin and a colorant. The process of toner preparation involves emulsion-aggregation which includes aggregating a mixture of an optional colorant, an optional wax, any other desired or required additives, and emulsions including the selected resins and optionally surfactants, and then coalescing the aggregate mixture (Zhou *et al.*, 2011).

One of the more recent newly developed methods for preparation of highly viscous organopolysiloxanes is via the manufacturing of highly viscous emulsions of a mixture of required components with an optional addition of an emulsifier. The resultant aqueous emulsions are highly viscous organopolysiloxanes, with reaction taking place as dispersion in water (Herzig & Dormeier, 2009).

POSS molecules also have the possibility of implementation in the field of film-forming and cosmetic emulsion compositions. Several compositions have been proposed for the film-forming and cosmetic compositions containing certain POSS and non-POSS silicone resins. New formulations have provided improved wear and pliability properties over the previously used silicone resin containing compositions. Wear property relates to how well a cosmetic retains its colour, coverage, texture and consistency over time. Pliability is the property applicable to film-forming cosmetics and is related to the brittleness of the film which, in turn, may impact on wear, appearance, texture and feel of the final product. Among others, the cosmetic compositions under discussion may be formulated as emulsions (Yu & Quadir, 2008).

In addition, some research has been conducted to investigate the incorporation of polyhedral oligomeric silsesquioxane molecules in combination with metal atoms or metal powders and polymeric or oligomeric carriers as neutron shielding into textile, garments and lotions. The main purpose was to provide a more effective shielding of living tissue from cosmic radiation during air or space flights. The ability of POSS nanomolecules to assist in uniform dispersion of metal atoms and metal particles with polymer in oil-based emulsions has also been demonstrated. Potential lotions considered within the framework of the study included both O/W and W/O emulsions (Lichtenhan *et al.*, 2009). Despite this investigation which focuses on highly concentrated explosive emulsions, there is enormous potential for further development and implementation within conceptually similar systems in such fields as food, cosmetics, pharmaceutical and biomedical industries.

CHAPTER 3

Materials and Methods

3.1 INTRODUCTION

This chapter presents the overview of methodologies and materials used in the experimental and analytical investigation of this study. The main goal was twofold: 1) to investigate the possibility of stabilisation of the highly concentrated emulsions (HCE) with the use of POSS nanomolecules, and 2) to investigate the effects of these compounds on stability of the system as compared to the one stabilised with the use of conventional PIBSA-Mea surfactant. Various hydrocarbon oils have been used as a media for the emulsion continuous phase to determine the effects of properties of the media on activity of the nanomolecules considered for this study. In addition, various types of POSS molecules with different functional groups have been used to ascertain the one most suitable for stabilisation of the system of interest.

Analytical investigations performed as part of the study are as follows:

- interfacial tension analysis;
- viscosity analysis of pure oils;
- microscopic analysis of resultant emulsions; and
- droplet size distribution analysis of resultant emulsions.

3.2 MATERIALS

All the materials used within this experimental work provided by African Explosives Limited and Lake International Technologies. A conventional oligomeric surfactant PIBSA-Mea was used as an emulsifier of choice. Additionally, seven types of POSS nanomolecules were used as stabilisers. Molecular structures of all the compounds are presented in subsequent sections. All of the compounds were soluble in hydrocarbon oils used as part of the continuous phase of emulsions.

3.2.1 PIBSA-Mea

PIBSA-Mea is a polyisobutylene succinic anhydride based surfactant with molecular weight of 1048, polar head group and non-polar hydrocarbon tail. Figure 3.1 illustrates the structure of the head group of PIBSA-Mea molecule.

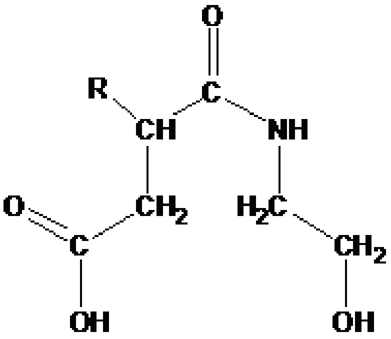


Figure 3.1: Head group structure of PIBSA-Mea molecule

The R-group represents polyisobutelene hydrocarbon. One of the possible conformations of the molecules of surfactant under discussion is illustrated in Figure 3.2. The concentration of the surfactant that was used in preparation of emulsions was 10% to the total weight of the oil phase, both when used solely and in combination with POSS nanomolecules.

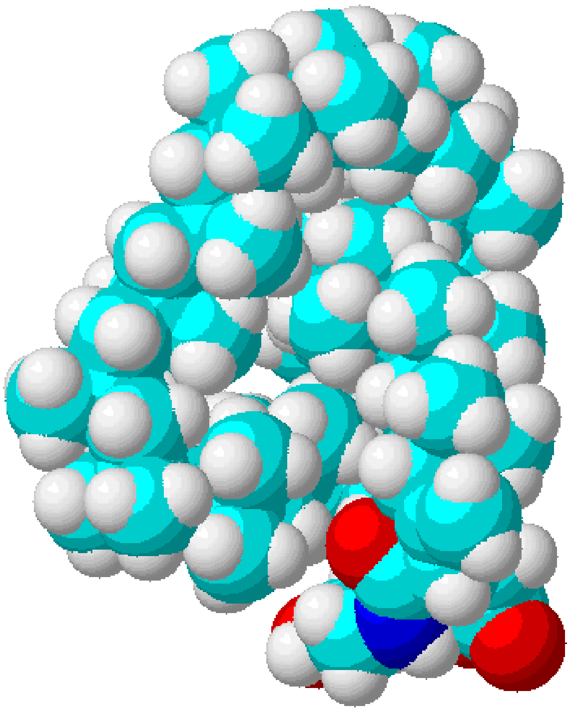
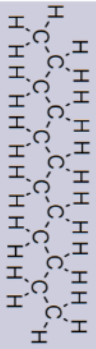


Figure 3.2: 3-D representation of the possible conformation of PIBSA-Mea molecule (with oxygen atoms presented in red, nitrogen in dark blue, carbon in light blue and hydrogen in white)

3.2.2 Hydrocarbon oils

Four types of hydrocarbon oils have been used as a media for the oil phase of the emulsions investigated: Ash-H, Mosspar-H, Parprol and Dodecane. The first three are industrial grade oils whereas the Dodecane used was a laboratory grade. Each of these oils possesses various polarity, viscosity and aromatic content properties. Table 3.1 presents a comparison of various properties of these oils as well as their compositions, where applicable.

Table 3.1: Comparison of content and properties of various hydrocarbon oils used in the study

Description	Mosspar-H	Ash-H	Parprol	Dodecane
iso-paraffins (%)	80 – 90	80 – 90	70	 $C_{12}H_{26}$
n-paraffins (%)	1 – 10	1 – 10		
cycloparaffins (%)	10 – 15	10 – 15		
naphthenics (%)	----	----	26	
aromatics (%)	0.04 (UOP495)	3.7 (UOP 495)	4 (ASTM D2140)	
Density at 20°C (kg/m^3)	795 (typical)	792 (typical)	866 (typical)	749 (typical)
Viscosity (cP)	3.1	3.4	51.6	1.4
Iterfacial Tension (mN/m)	23.7	19.3	8.1	25.3

3.2.3 POSS nanomolecules

POSS nanomolecules used as stabilisers in this study have the general structure presented in Figure 3.3. Molecules adopt the structure of an inorganic cage consisting of silica and oxygen with various functional groups grafted on it. Some of these functional groups carry the function of assisting with solubilisation and are otherwise non-reactive. Still others, on the other hand, are present particularly for the purpose of making the molecule reactive with compounds of interest. Within the frame of this current study were seven different types of nanomolecules with various reactive functional groups. These functional groups (X) along with their respective POSS names and molecule types and codes adopted in the investigation are presented in Table 3.2.

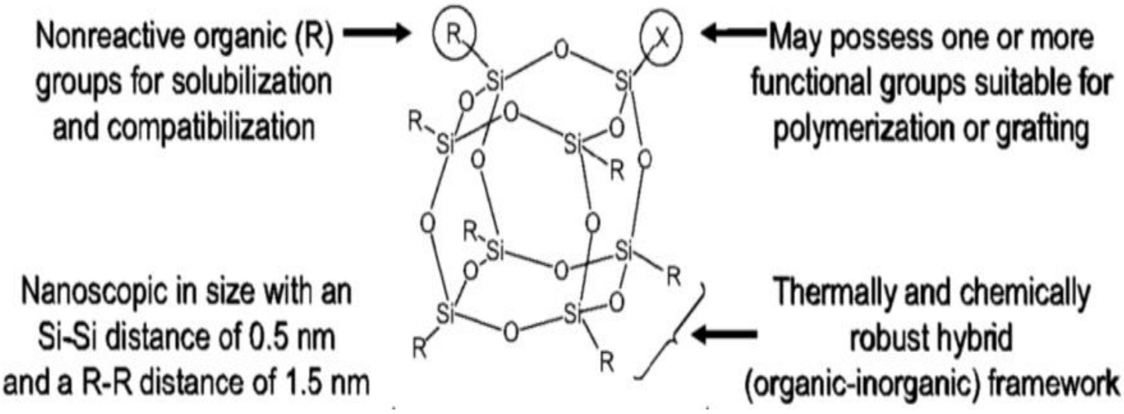
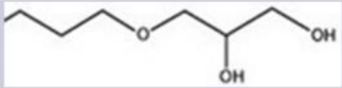
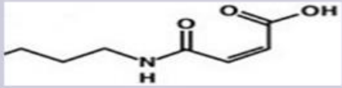
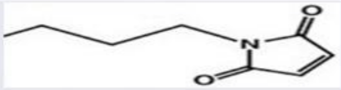
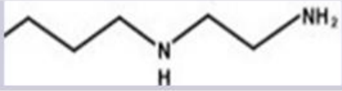


Figure 3.3: General molecular structure of POSS compound

Table 3.2: Reactive functional groups, codes, types and names of POSS nanomolecules used in the investigation

Reactive Functional Group	Code/Type	Name
	AL0130/Alcohol	1,2 – propanediolisobutyl
	MA0701/Acrylate	acryloisobutyl
	CA0296/Carboxylic Acid	maleamic acid-isobutyl
	IM0673/Imide	maleimide isobutyl
	AM0265/Amine	aminopropylisobutyl
	AM0270/Amine	aminopropylisooctyl
	AM0275/Amine	aminoethylaminopropylisobutyl

It is important to note that for six out of seven molecules, the non-reactive R-group was the short chain i-butyl group. Only in the case of AM0270, this group was a longer chain length i-octyl. All of the molecules considered were soluble within the hydrocarbon oils used. When used solely, the concentration of the compound taken was 6% by weight to the total amount of the oil phase of emulsion.

3.3 METHODOLOGY

3.3.1 Droplet size distribution analysis

Measurements of the size of dispersed particles were carried out with the Mastersizer-2000 device (Malvern Instruments Co) (Figure 3.4). The measuring procedure is based on sample dispersion under software control and the measurement of angle dependence of the intensity of scattering of a collimated He-Ne laser beam. Particle size in the range from 0.26 to 1500 microns can be measured; this range is much wider than sizes of the real samples used in this work. The sized distribution calculations are based on the rigorous Mie theory using the standard software applied to the instrument. Each emulsion sample (small quantity of sample taken) was dispersed in the large volume of oil to attain a very dilute concentration of water droplets in oil and to avoid agglomerates formation. The average value D_{32} was used as a measure of droplet size in the investigation, with an accuracy measurement of 99%.

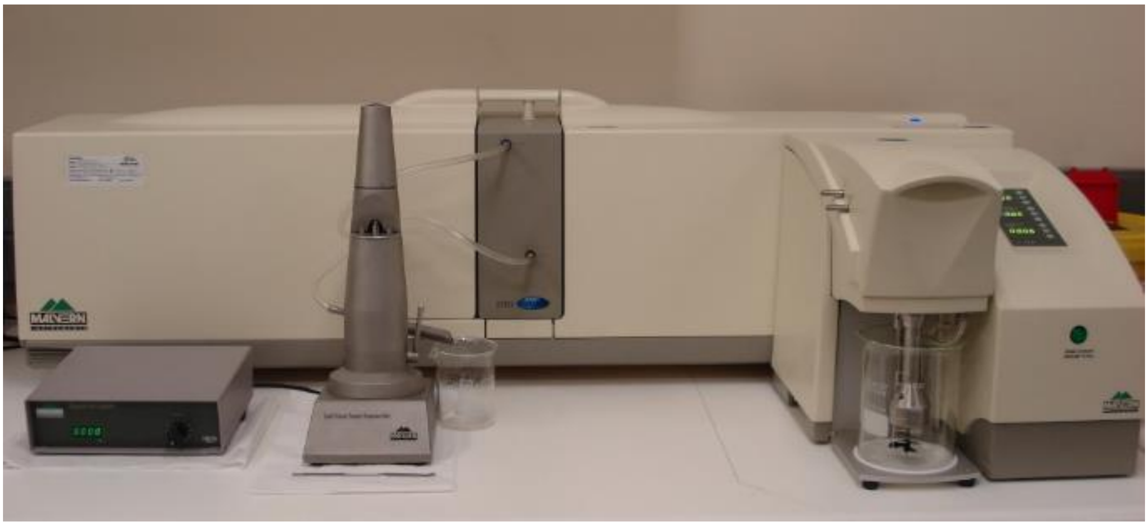


Figure 3.4: Mastersizer-2000 used for performing droplet size distribution investigation

3.3.2 Optical analysis

The optical analysis was conducted using visual observation for the analysis of structural changes of the materials at different emulsion formulation content and for analysis of size, shape and degree of crystallinity. This was carried out with a Leica optical microscope (Figure 3.5) equipped with a digital camera, at a magnification of 40x.

Figure 3.5: Leica optical microscope

3.3.3 Rheological investigation

The rheological experimental methods are based on measuring the rheological properties. This was performed using the Rotational Rheometer MCR-300 (‘Paar-Physica’, Germany) (Figure 3.6). Wide ranges of shear rates (from app. 10-4 to 103 s^{-1}) and shear stresses are available for investigation which allows for data acquisition on rheological properties in a very wide spectre. This instrument can also operate in a wide range of frequencies, from 10^{-3} up to 102 Hz. In this oscillating mode of deformations, dynamic modules are measured as a function of frequency. In addition, the amplitude of deformations can vary between 0.01% all the way to several hundred percent. Instrument measurement facilities are supported with modern software, which includes many applied programmes.

In the scope of this current investigation, measurements performed using these methodologies were for the purpose of measuring the viscosity of the oils. To eliminate uncertainty arising from fluctuating temperature of the laboratory environment, all measurements were conducted at 25°C.

Figure 3.6: Rotational rheometer Paar Physica MCR-300

3.3.4 Interfacial properties investigation

The dynamic interfacial tension and interfacial moduli were determined using a PAT 1 tensiometer supplied by Sinterface Technologies, Berlin, Germany (Figure 3.7). The basic operational principle of this instrument is that the Young-Laplace equation is fitted to the profile of an image of a droplet in the more dense phase suspended in the less dense phase from a capillary. The Young-Laplace equation balances the interfacial tension against gravity, with the interfacial tension tending to reduce the interfacial area and gravity tending to increase it by extending the droplet. This balance leads to certain practical considerations concerning the capillary diameter and the droplet volume. For example, if the droplet volume is too low, the interfacial tension dominates and the droplet assumes a spherical shape from which the interfacial tension cannot be extracted. If the droplet volume is too high, gravity dominates and the droplet detaches from the capillary.

A quartz cuvette is filled with a denser phase, which in the case of current investigation, was hydrocarbon oil containing various POSS nanomolecules dissolved within at a concentration of 1% by weight. A capillary nozzle was then placed from the top into the solution following the introduction of a less dense phase. The less dense phase, used for measurements, was a 40% solution of laboratory grade ammonium nitrate. A pear-shaped droplet of this solution in the oil phase was formed, at which point the analysis commenced. Each analytical run was set up at 15000 seconds to allow for the system to equilibrate.

Figure 3.7: Sinterface Technologies PAT 1 tensiometer

In addition, interfacial tension measurements were performed using the Kruss K100 tensiometer (Figure 3.8) with principles of measurements based on the Wihelmy slide method. This was for comparison purposes of the results obtained from two different in principle interfacial tension measurement techniques.

Figure 3.8: Kruss K100 tensiometer

Approximately 15 cm^3 of a 60% laboratory grade ammonium nitrate solution was placed in a clean 70 mm diameter glass dish. A hydrophilic platinum plate was then suspended vertically from a sensitive force transducer with its lower edge penetrating the surface of the ammonium nitrate solution. Following this was a gradual addition of approximately 50 cm^3 of the oil phase containing 1% by weight of POSS nanomolecules until the plate was fully submerged. Measurements were then initiated, with each measurement set up at 10800 seconds to allow the system to come to equilibrium.

3.3.5 Emulsion preparation

The small batch sample preparation was performed using a Silverson L4RT dispergator (Figure 3.9) at a constant agitation rate of 2500 revolutions per minute. Slow addition of aqueous phase into the oil phase was performed under ambient conditions with constant agitation of the system for successive emulsification. The dispersed phase of emulsion comprised 60% by weight aqueous solution of industrial grade ammonium nitrate. The continuous phase was a solution of various oils and POSS nanomolecules within the scope of investigation at a concentration of the latter of 6% by weight to the total amount of oil phase. The target dispersed phase concentration of each sample was set at 90% by weight of the total mass of the sample.

Figure 3.9: Silverson L4RT dispergator

Preparation of the bulk emulsion was performed using the Hobart N50 mixer (Figure 3.10). The mixer consists of an agitator unit and a bowl heated to 85°C. The emulsification process includes gentle pouring of pre-dissolved ammonium nitrate solution into the surfactant in the continuous phase solution contained in the bowl. The mixing performance of Hobart was facilitated by intensive shearing of the sample between the agitator and the bowl. The aqueous phase used for preparation of bulk emulsion was 80% solution of industrial grade ammonium nitrate. This required heating to 80ºC for successive dissolution of ammonium nitrate. The solution was then immediately added into the pre-heated bowl containing the oil phase, and the process was continued by slow mixing. After the transfer was complete, the system was subjected to high intensity shearing for formation of emulsion and further refinement to the desired droplet size. Oil phase of emulsion contained 10% by weight PIBSA-Mea surfactant in combination with 0.1% by weight of POSS molecules. The reference sample contained 10% of PIBSA-Mea emulsifier solely.

Figure 3.10: Hobart N50 mixer

After preparation, the sample was left to slowly cool to ambient temperature, after which it was subjected to further analysis.

3.3.6 Emulsion shearing

In order to investigate the under shear stability of the resultant system, it was subjected to high stress shear with the use of a double cylinder pumping setup as illustrated in Figure 3.11. The two cylinders are separated and emulsion is transferred from one into the other through a 4mm hole, performed at a pressure of one bar. This procedure mimicked the industrial pumping conditions within the confined laboratory environment.

Figure 3.11: Double cylinder pumping setup

CHAPTER 4

Results and Discussions

4.1 EFFECT OF POSS NANOMOLECULES ON THE INTERFACIAL PROPERTIES IN HIGHLY CONCENTRATED EMULSIONS

This section presents the results and interpretations of an investigation of the effect of POSS nanomolecules on the interfacial tension at the planar aqueous-oil interface as well as the interfacial elasticity within the system under investigation.

The primary intent of this part of the present investigation is to determine whether the POSS nanomolecules under investigation occupy aqueous-oil interface and hence are surface active. In addition, results also illustrate which types of these molecules are more surface active than others.

It is important to note that the oil phase contained only POSS nanomolecules as a stabilising agent. No additional surfactants were present.

4.1.1 Effect on the interfacial tension

We first look at the effect of the addition of various POSS nanomolecules on the interfacial tension across the plane interface of the two immiscible liquids. Interfacial tension measurements were performed using a Krüss K100 tensiometer, supplied by Krüss Gmbh, Germany. The oil phase comprised dilution of 1% of POSS nanomolecules within various hydrocarbon oils investigated (see Chapter 3: Materials and Methods). The aqueous phase was a 60% solution of laboratory grade ammonium nitrate. All measurements were conducted at 30^{o}C to eliminate the possible uncertainty in the experimental results arising from fluctuations of ambient temperature within the laboratory environment. Results of all measurements are presented in Table 4.1. In addition, performed and presented for the comparison properties are the interfacial tension values measured for the system comprising pure oils without any nanomolecules or other types of stabilisers present.

As seen from the interfacial tension results obtained, the addition of POSS nanomolecules to the oil phase leads to the decrease of interfacial tension between the two immiscible liquids under investigation. This is true for all combinations of POSS molecules with oils across the matrix of samples. This is an indication of two things: that all POSS molecules under investigation 1) are indeed surface active in all taken oils independently of the oil properties, and 2) do occupy the interface between the phases, resulting in the drop of interfacial tension.

Table 4.1: Interfacial tension values at the planar aqueous-oil border for a series of POSS nanomolecules and hydrocarbon oils under investigation

POSS Type	Interfacial Tension, γ (mN/m)			
	Mosspar - H	**Ash-H**	**Parprol**	**Dodecane**
Pure Oil	23.7	19.3	8.1	25.3
AL0130	19.7	17.4	2.8	16.9
MA0701	10.0	11.7	8.7	25.2
CA0296	16.1	15.6	----	----
IM0673	16.2	17.8	16.7	19.4
AM0265	6.4	6.6	9.0	7.2
AM0270	8.7	8.4	11.6	9.0
AM0275	3.3	3.8	2.8	6.3

The largest drop of interfacial tension for all considered oils is observed with POSS nanomolecules containing amine functional group as compared to all the other types of molecules investigated. In particular, the most significant decrease of interfacial tension results from the addition of molecules with both secondary and primary amine within their functional group, AM0275. The presence of these nanomolecules resulted in the gelation effect occurring across the aqueous-oil interface with subsequent formation of flexible gel layer, as illustrated in Figure 4.1.

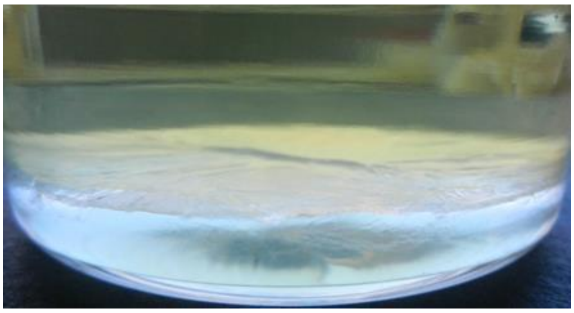


Figure 4.1: Gel layer formation across the aqueous-oil interface resulting from addition of AM0275 POSS nanomolecules to the oil

It is important to note that POSS molecules containing the carboxylic acid functional group, CA0296, were excluded from the investigation at a certain point of the experiment, because of the gelation of these molecules that occurs within the oil phase which renders any accurate analytical analysis impossible. This phenomenon will be scrutinised in more detail in upcoming sections.

4.1.2 Effect on the interfacial elasticity

In this section, we look at the effect of the addition of various POSS nanomolecules on the interfacial elasticity that was obtained using a PAT 1 tensiometer supplied by Sinterface Technologies, Berlin, Germany. As for the interfacial tension measurements, the oil phase was comprised of dilution of 1% of POSS nanomolecules within various hydrocarbon oils investigated (see Chapter 3: Materials and Methods). The aqueous phase, on the other hand, was a further diluted 40% solution of laboratory grade ammonium nitrate. All measurements were conducted at ambient laboratory temperatures of approximately 25^{o}C, as opposed to interfacial tension measurements: interfacial elasticity is not highly dependent on temperature and prone to uncertainty in measurements resulting from temperature fluctuations. In addition these experiments were conducted to support outcomes obtained during interfacial tension measurements; hence we are only interested in the general trends rather than exacting numerical data. With this in mind, experimental results are presented in Table 4.2. This table contains results obtained at the frequency of oscillation of 1 Hz for Mosspar-H and Ash-H oils.

No accurate consistent measurements were possible in the industrial grade Parprol oil and laboratory grade Dodecane; this was true for all the POSS nanomolecules across the matrix of samples. In the case of Parprol, drop formation was possible; however, due to the very high viscosity of this oil, it was impossible to form and maintain the drop of the required shape that is necessary for successive measurements. For laboratory grade Dodecane, once again, drop formation was possible at equilibrium; however, extreme instability of the formed drop was observed during oscillation which resulted in a constant drop detachment from the capillary nozzle and hence interruption of experiment. It is also imperative to note that in the experimental system comprising pure oil without any stabilisers present, at oil phase, no drop formation is possible regardless of the type of oil used. In these scenarios, there is a complete inability of formation of drop that is stably attached to the capillary nozzle, even at the complete equilibrium of the system. Hence, even given that no experimental data collection was possible in Parprol oil and Dodecane, the fact of possibility of drop formation at equilibrium state of the system is already an indication of POSS nanomolecules surface activity.

Table 4.2: Interfacial elasticity values for a series of POSS nanomolecules in Mosspar-H and Ash-H oils measured at oscillation frequency of 1 Hz

POSS Type	**Interfacial Elasticity, E' (mN/m)**	
	Mosspar - H	**Ash-H**
AL0130	5.73	6.69
MA0701	----	8.27
CA0296	20.61	24.93
IM0673	25.06	29.41
AM0265	2.06	----
AM0270	5.49	8.52

An examination of results obtained indicates the varying interfacial elasticity dependent on the type of POSS nanomolecules present in the system. This result supports the outcome obtained as part of the interfacial tension measurements pointing to the fact that nanomolecules under investigation are indeed surface active, and the degree of this activity is directly dependent on the type of functional group present in the molecules.

It was impossible to perform measurements for the system comprising POSS molecules with the acrylate functional group, MA0701, in the low viscosity and low aromatic content Mosspar-H oil. This was due to extreme instability of the drop during the oscillation. Nevertheless, drop formation at equilibrium state of the system was possible, indicating a low activity of these molecules at the interface.

The gelation effect at the interface of the two immiscible phases observed during the interfacial tension measurements for the amine POSS molecules, AM0275, became especially pronounced during the interfacial elasticity measurements. Gelation took place immediately upon the entrance of the ammonium nitrate solution into the oil phase containing these molecules. The formed gel-like barrier at the interface was rigid, prohibiting the even formation of the drop of its required spherical or pear shape, as illustrated in Figure 4.2. Any interfacial elasticity measurements and further analysis became impossible to perform because of this phenomenon. The same was observed for the amine POSS molecules, AM0265, in the system with the low viscosity and high aromatic content Ash-H oil.

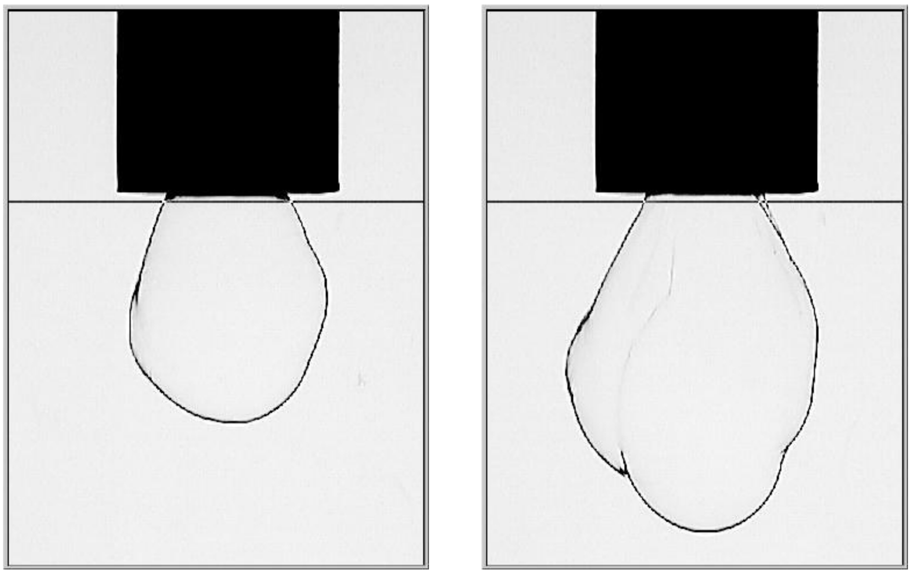


Figure 4.2: Gel-like layer at the interface between the two phases prevents formation of an even shaped droplet required for successive analysis

The gel-like film formed at the interface fully encapsulated the ammonium nitrate within preventing any access inside from the outward environment and vice versa. Any escape of ammonium nitrate into the environment was impossible since immediate gelation of the solution occurred, keeping the layer integral. This is illustrated in Figure 4.3, showing the individual encapsulated detached droplets stacked at the bottom of the cuvette containing the oil phase.

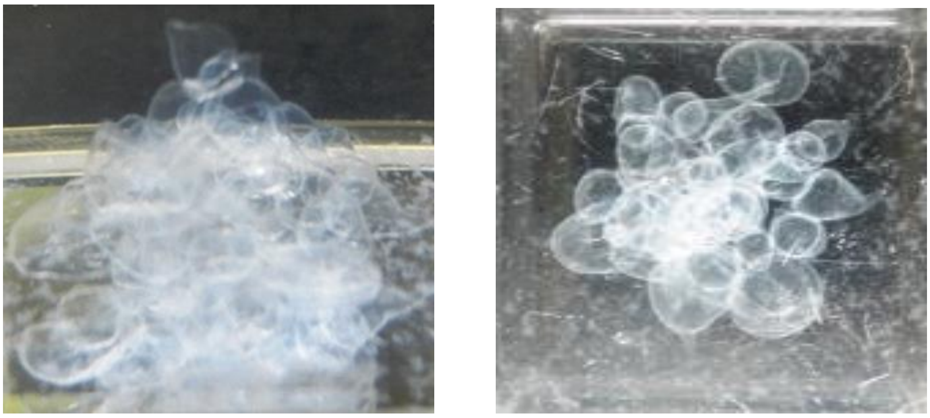


Figure 4.3(a): Encapsulated ammonium nitrate droplets stacked in the cuvette containing the oil phase comprising AM0275 POSS as a stabiliser

Importantly, despite of gelation of the interface of a drop resulting in encapsulation, the ammonium nitrate within remained in its initial liquid solution state. No gelation took place inside the drop beyond the interfacial gel-like layer.

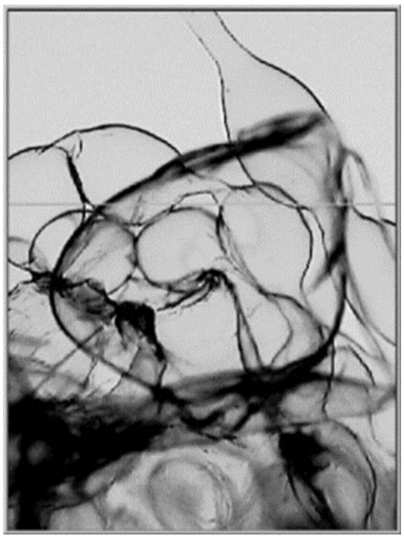


Figure 4.3(b): Encapsulated ammonium nitrate droplets stacked in the cuvette containing the oil phase comprising AM0275 POSS as a stabiliser (captured with instrument camera)

This has been proven by sucking the solution out of the encapsulated drop while it was still attached to the capillary nozzle. The liquid solution inner got sucked back successfully, leaving the empty gel-like bag attached to the nozzle. This also illustrates the rigidity of the gel-like outer interface formed surrounding the droplet. The result of this experiment is demonstrated in Figure 4.4.

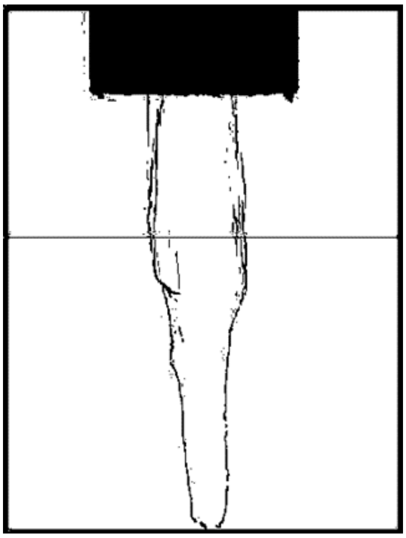


Figure 4.4: Empty gel-like bag formed at the interface of two immiscible liquids in the presence of AM0275 POSS molecules within the oil

4.2 EFFECT OF POSS NANOMOLECULES ON THE VISCOSITY OF OIL PHASE IN HIGHLY CONCENTRATED EMULSIONS

In this section we investigate whether or not the addtion of POSS nanomolecules has any notable effect on the viscosity of the oil phase and if it does, if this effect is independent of the type of functional group molecules posses or if different functional groups will affect the viscosity to various extents.

Viscosity measurements were conducted using an MCR-300 rotational Rheometer, supplied by 'Paar-Physica', Germany. As for the interfacial tension measurements, the oil phase comprised dilution of 1% of POSS nanomolecules within various hydrocarbon oils investigated (see Chapter 3: Materials and Methods). Since liquid viscosity is highly dependent on temperature, to eliminate any possible uncertainty in the experimental results arising from fluctuations of ambient temperature within the laboratory environment, all measurements were conducted at 25°C, results of which are presented in Table 4.3, including viscosity measurements performed for pure oils under investigation.

Table 4.3: Interfacial elasticity values for a series of POSS nanomolecules in Mosspar-H and Ash-H oils measured at oscillation frequency of 1 Hz

POSS Type	**Viscosity (cP)**			
	Mosspar-H	**Ash-H**	**Parprol**	**Dodecane**
Pure Oil	3.1	3.4	51.6	1.4
AL0130	3.2	3.5	54.8	1.5
MA0701	3.0	3.8	53.6	1.7
CA0296	----	----	----	----
IM0673	3.4	3.7	54.0	1.2
AM0265	3.8	3.1	52.9	1.5
AM0270	3.2	3.5	54.1	1.5
AM0275	3.6	3.5	55.1	1.5

An examination of results obtained clearly indicates that the addition of POSS nanomolecules into the oil does not have any major affects on the oil viscosity. This is true for all combinations of nanomolecules with oils investigated in this study. This finding is also true for the concentration of POSS molecules present in the oil within the scope of this study. The addition of higher concentrations of molecules into oils may result in a change of oil viscosity; this, however, falls outside the scope of this study and hence it is assumed for the purposes of the study that no such effect takes place.

As mentioned previously, POSS nanomolecules containing the carboxylic acid functional group, CA0296, were excluded from the investigation. This was due to gelation of these molecules that occurred within the oil phase, as illustrated in Figure 4.5. For viscosity measurements, this effect rendered any analysis and measurements impossible across the matrix of samples regardless of properties of oil used as media for dissolution. Slow gelation within the oil phase caused constant change of viscosity in the progress of the experiment; in addition, gelation did not occur as an even gelation throughout the whole of oil phase. In fact, contrary to this, an uneven formation of gel clusters took place in oil.

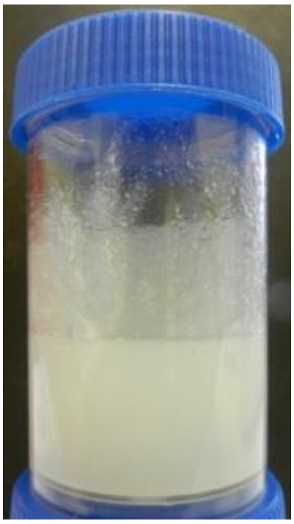


Figure 4.5: Gelation taking place within the oil phase containing carboxylic acid, CA0296, POSS nanomolecules

It is important to note that dissolution of this type of molecule required elevated temperature of 110°C. Gelation within the oil commenced immediately on the cool down of the media after dissolution of molecules occurred. A further investigation was conducted to determine the effect of nanomolecule concentration, within the oil, on gelation. This was performed within the low viscosity and low aromatic content Mosspar-H oil at CA0296 concentrations of 0.5%, 1%, 2% and 6%. It was found that gelation within the oil phase took place at all concentrations; however, the temperature at which this effect commenced, as well as the rate of gelation, were both directly proportional to the concentration of molecules within the phase: the lower the concentration of molecules, the lower the temperature at which gelation commences and the slower the rate of gelation and vice versa.

4.3 ABILITY OF POSS NANOMOLECULES TO FORM AND STABILISE HIGNLY CONCENTRATED EMULSIONS

This section presents the results and interpretation of an investigation of the ability of POSS nanomolecules towards the formation and stabilisation of highly concentrated emulsions solely without the presence of any additional surfactant within the system.

The purpose of this section is to determine if any of the investigated molecules are able to stabilise a system of interest, and furthermore, to determine which types, hence the presence of which functional group in the molecule will affect an ability to form and better stabilise this system. All samples were prepared at a constant shear of 2500 revolution per minute using a L4RT high-speed mixer supplied by Silverson. The concentration of nanomolecules within the oil phase was set at 6%. The target dispersed phase concentration was 90% by weight and the ammonium nitrate concentration within the dispersed phase was 60% by weight. This concentration was chosen for the purposes of performing all the experiments at ambient room temperatures since a small batch samples were prepared. Higher concentrations of ammonium nitrate within the solution require elevated temperatures for emulsion formation for ammonium nitrate to remain in the solution and not crystallise out from oversaturation. Keeping the system at an elevated temperature throughout the experiment is only possible with the preparation of bulk amounts of samples due to equipment limitations.

In the cases when emulsion does not reach the target dispersed phase concentration, one of two things occur at any concentration prior to target: 1) phase separation back into oil phase, or aqueous phase or 2) phase inversion. *Phase inversion* is the phenomenon of dispersed phase and continuous phase switching, and in our case, emulsion becoming oil-in-water type from water-in-oil. This phenomenon is most common within the system under investigation, and unless otherwise explicitly stated, is assumed to have occurred in the investigation. The concentration of dispersed phase at which phase inversion takes place is referred to as *inversion point* and is reported in percentage dispersed phase added to the system. This concentration was monitored and recorded as an indication that the system did reach high enough dispersed phase concentrations and could indeed be treated as a highly concentrated emulsion. It is crucial to keep in mind that for a small batch system – a smaller scale with a more dilute ammonium nitrate solution as dispersed phase – it is common for inversion to take place. Therefore, for the purposes of this investigation, it was not critical for the system to reach a target concentration as far as inversion point occurring at dispersed phase concentrations of over 75%. In addition, as will be seen in subsequent sections, there is no relation between the inversion point and system stability. Higher inversion points or samples reaching the target concentration may be determined to be highly unstable, and vice versa.

Droplet size distribution measurements for all prepared samples were performed at 2000 revolutions per second using the Mastersizer-2000 supplied by Malvern Instruments Co. Droplet size distribution is an indication of the average size of the droplets of dispersed phase within the analysed sample. Hence, data obtained from that technique gives an indication of droplet coalescence within the system, and the rate of this coalescence may be followed. For our system, and particularly for the purposes of the current section, an indication of the stability of the system is an average droplet size in the region of 10 to 20 microns. A shift of average droplet size into the larger region is an indication of coalescence taking place within the sample and therefore the instability of the system.

All the microscopic observations were performed at magnification 40x using an optical microscope supplied by Leica. This was done to both support the data obtained using droplet size distribution measurements as well as to visually asses the quality of the sample and possible crystallisation occurring that is generally not detected by droplet size distribution measurements.

Each of the following sub sections focuses on one type of nanomolecule investigated.

4.3.1 Alcohol POSS nanomolecules

We first look at nanomolecules containing alcohol functional group, 1,2: propanediolisobutyl POSS (AL0130). These molecules contain i-butyl R-group and have a molecular formula $C_{34}H_{76}O_{15}Si_8$.The molecular structure of this compound is illustrated in Figure 4.6. A summary of results obtained is shown in Figure 4.7. As can be seen, emulsion formation was possible *only* for the systems that contained low viscosity and aromatic content Mosspar-H as well as low viscosity and high aromatic content Ash-H oils.

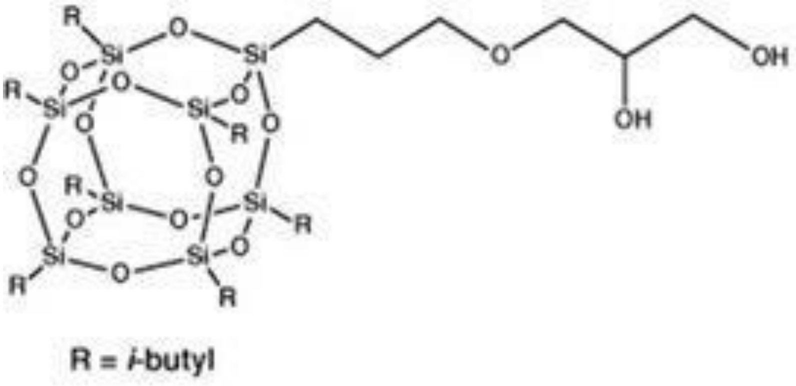


Figure 4.6: 1,2 – propanediolisobutyl POSS molecular structure

The inversion point for these two samples occurred at approximately the same concentrations, 82.5% and 86.9% respectively, and in both cases close to the target concentration of 90%. No emulsion formation was possible for the samples prepared using high viscosity high aromatic content Parprol oil or laboratory grade Dodecane. In both cases, no phase homogenisation took place from the initial point of sample preparation

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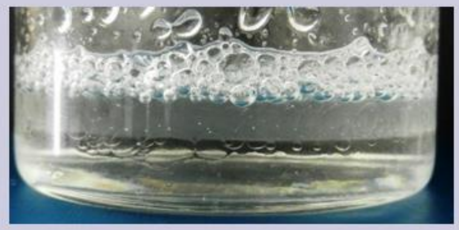
Oil	Emulsion	Inversion Point (%wt)	Stability	Microscopy
Mosspar - H		82.5	Immediate significant coalescence Separation – 30 minutes	Impossible to obtain. Emulsion breaks down to water and oil under shear
Ash - H		86.9	Immediate significant coalescence Separation – 30 minutes	Impossible to obtain. Emulsion breaks down to water and oil under shear
Parprol	No emulsion formation is taking place. Phases do not homogenize within each other.	 🚫		
Dodecane				

Figure 4.7: Overview of the data obtained for the samples prepared using alcohol POSS nanomolecules

In terms of stability, both successfully formed samples proved to be highly unstable with the immediate coalescence that occurred after preparation. This was followed by the complete phase separation within the first 30 minutes from preparation. Droplet size distribution curves illustrating coalescence within the investigated samples are shown in Figure 4.8. Examination of this data indicates a higher degree of coalescence occurring in the sample prepared using the Ash-H oil. However, given the overall high degree of instability of both samples, this can be considered an insignificant difference. Microscopy of the samples was impossible to obtain due to extreme instability of both samples under shear. Any attempt of microscopic slide preparation for analysis resulted in, once again, complete emulsion phase separation.

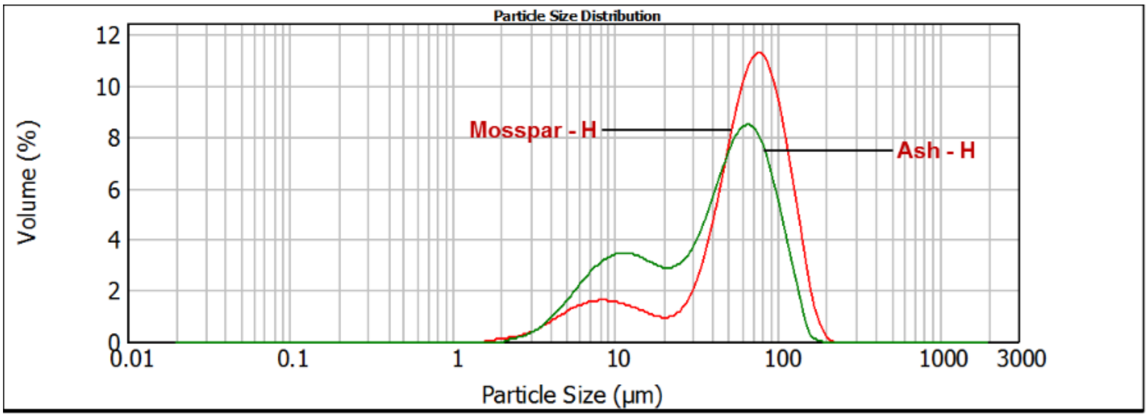


Figure 4.8: Droplet size distribution curves for the samples prepared using alcohol POSS nanomolecules with Mosspar-H and Ash-H oils

From the results obtained experimentally and discussed above, it is clear that 1,2 – propanediolisobutyl POSS contains an extremely low capacity towards the formation and further stabilisation of the system of interest. This is especially true for highly viscous and pure laboratory grade oils used as the media of the continuous phase of emulsion. This is an indication, then, of a high degree of incompatibility, in the form of extremely low reactivity of the alcohol functional group contained within these molecules, with the dispersed phase of the system under investigation, resulting in low to no stabilisation of the aqueous-oil interface within the emulsion and leading to immediate high degrees of coalescence, and complete instability under shear of the successfully formed samples. This ultimately resulted in complete emulsion separation shortly after sample preparation.

4.3.2 Acrylate POSS nanomolecules

In this sub section we investigate nanomolecules containing the acrylate functional group acryloisobutyl POSS (MA0704). These molecules contain i-butyl R-group and have a molecular formula $C_{34}H_{72}O_{14}Si_8$. The molecular structure of this compound is illustrated in Figure 4.9.

A summary of results obtained is presented in Figure 4.10. No emulsion formation was possible for any of the systems under consideration. This was independent of type and properties of oils used within the continuous phase of the system. In all instances, no phase homogenisation took place from the initial point of sample preparation.

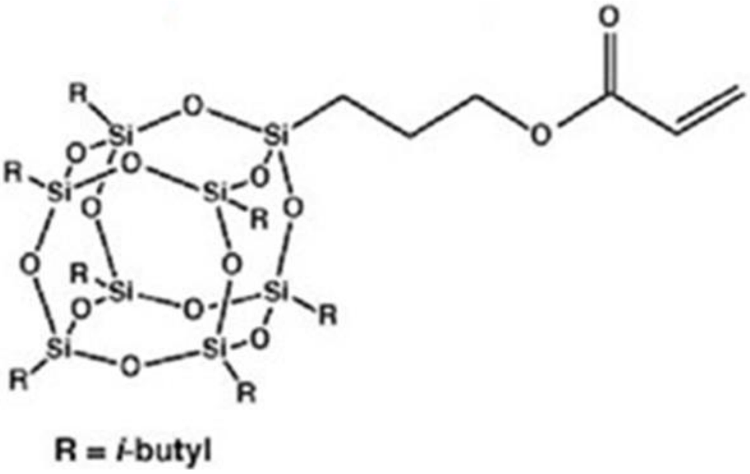


Figure 4.9: Acryloisobutyl POSS molecular structure

From the results obtained experimentally, it is clear that acryloisobutyl POSS (MA0701) nanomolecules are completely unable to form a highly concentrated emulsion when used as a stabilising agent. This is true for all of the types of oils used as part of continuous phase in this investigation regardless of properties such as viscosity and aromatic content. We can conclude that the acrylate functional group contained within the investigated molecules is completely incompatible with both the dispersed phase and the system of interest as a whole.

A complete inability towards the stabilisation of the interface between two immiscible phases indicates a complete absence of reactivity between the molecules and dispersed phase of the system. In addition, the independence of the result from the oil type and properties indicates a complete absence of reactivity and any degree of interactions between the molecules and the oil phase.

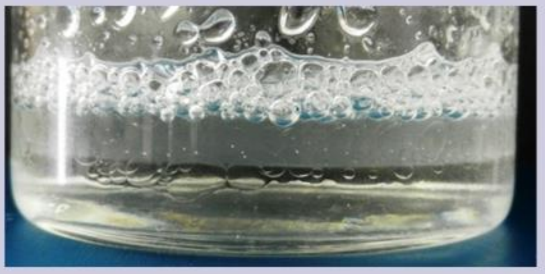
Oil	Emulsion	Inversion Point (%wt)	Stability	Microscopy
Mosspar - H	No emulsion formation is taking place. Phases do not homogenize within each other.	🚫 		
Ash - H				
Parprol				
Dodecane				

Figure 4.10: Overview of the data obtained for the samples prepared using alcohol POSS nanomolecules

4.3.3 Carboxylic acid POSS nanomolecules

Here we look at the nanomolecules containing carboxylic acid functional group, maleamic acid-isobutyl POSS (CA0296). These molecules contain i-butyl R-group and have a molecular formula $C_{35}H_{73}NO_{15}Si_8$. The molecular structure of the compound is illustrated in Figure 4.11.

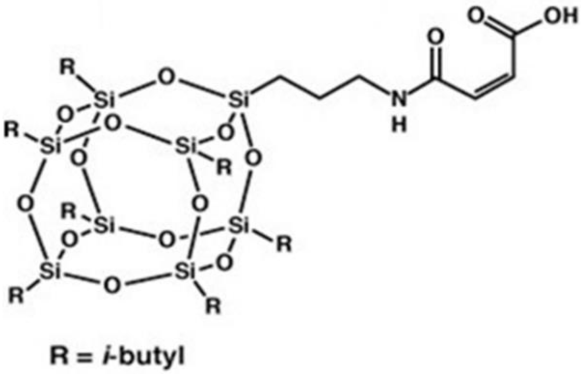
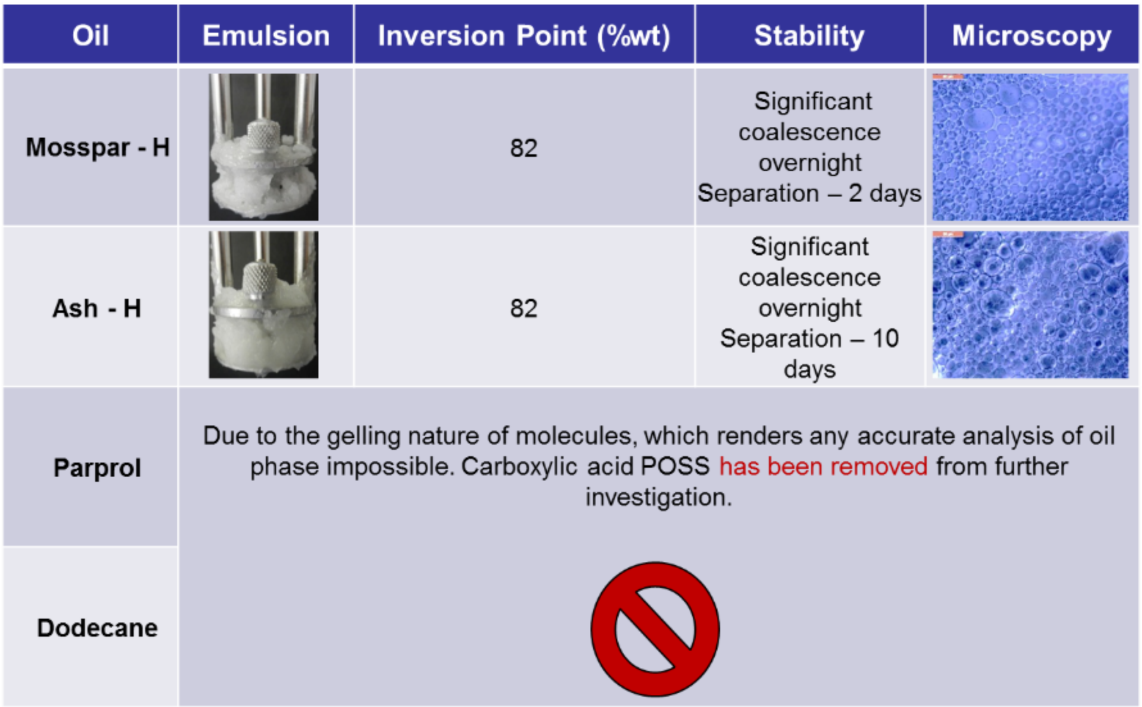


Figure 4.11: Maleamic acid-isobutyl POSS molecular structure

As was mentioned previously, the gelation of POSS nanomolecules containing carboxylic acid functional group occurred within the oil phase, rendering accurate analysis, investigation and conclusions impossible. This effect was independent of the oil properties or POSS concentration within the oil phase. Due to this phenomenon, only two sets of samples have been prepared and studied, emulsions containing Mosspar-H and Ash-H as part of their respective oil phases. After this, CA0296 nanomolecules were excluded from further investigation. An overview of the experiments conducted with these molecules is presented in Figure 4.12.

As can be seen, emulsion formation was possible for both low viscosity and aromatic content Mosspar-H oil as well as low viscosity with high aromatic content Ash-H oil.



Oil	Emulsion	Inversion Point (%wt)	Stability	Microscopy
Mosspar - H		82	Significant coalescence overnight Separation – 2 days	
Ash - H		82	Significant coalescence overnight Separation – 10 days	
Parprol	Due to the gelling nature of molecules, which renders any accurate analysis of oil phase impossible. Carboxylic acid POSS has been removed from further investigation. 🚫			
Dodecane				

Figure 4.12: Overview of the data obtained for the samples prepared using Maleamic acid-isobutyl POSS molecules

The inversion point for both emulsions occurred at 82% by weight of ammonium nitrate solution added. In terms of stability, both samples demonstrated low stability with significant coalescence occurring overnight. Figure 4.13 demonstrates droplet size distribution for the freshly prepared sample as well as overnight with microscopy for both.

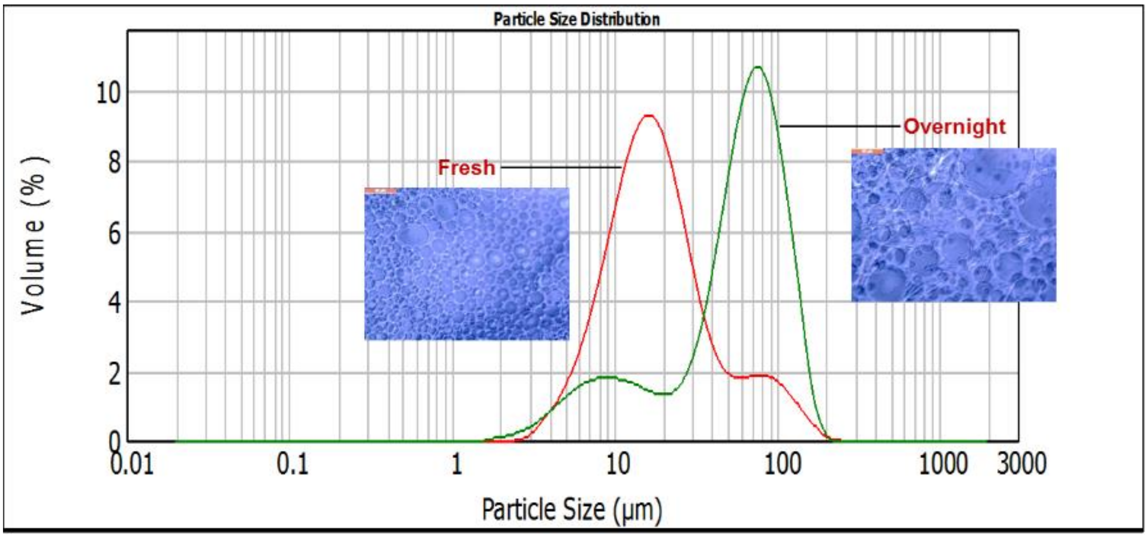


Figure 4.13: Droplet size distribution curves and respective microscopic images for the sample prepared using carboxylic acid POSS nanomolecules with Mosspar-H oil

It is clearly evident from droplet size distribution curves that significant coalescence is taking place within the sample. A shift of the average droplet size is observed from the 10 micron region for the freshly prepared sample into predominantly the 100 micron region for the same sample analysed the following day after preparation. This result is supported by the microscopic investigation from which coalescence within the emulsion is also clearly observed. Furthermore, this sample underwent a complete phase separation two days after preparation.

Experimental results for emulsion prepared using the low viscous high aromatic content Ash-H oil indicate a slightly higher overall stability to separation with time. Nevertheless, rapid significant coalescence was observed in this sample, indicated by both droplet size distribution curves and the microscopic observations (Figure 4.14). It can be seen that the following day after sample preparation, coalescence within the emulsion was already strongly evident and by Day 3, a complete shift of the average droplet size took place from the 10 micron region into the 100 micron region. These results are in full agreement with supporting microscopic investigation of the sample. It is important to note that emulsion became too unstable under shear and any attempts of microscopic slide preparation after the Day 4 ageing point led to a complete sample phase separation on the slide into oil and water. Droplet size distribution investigation was possible up until Day 8 of sample ageing. A complete sample separation into aqueous and oil phase took place by Day 10.

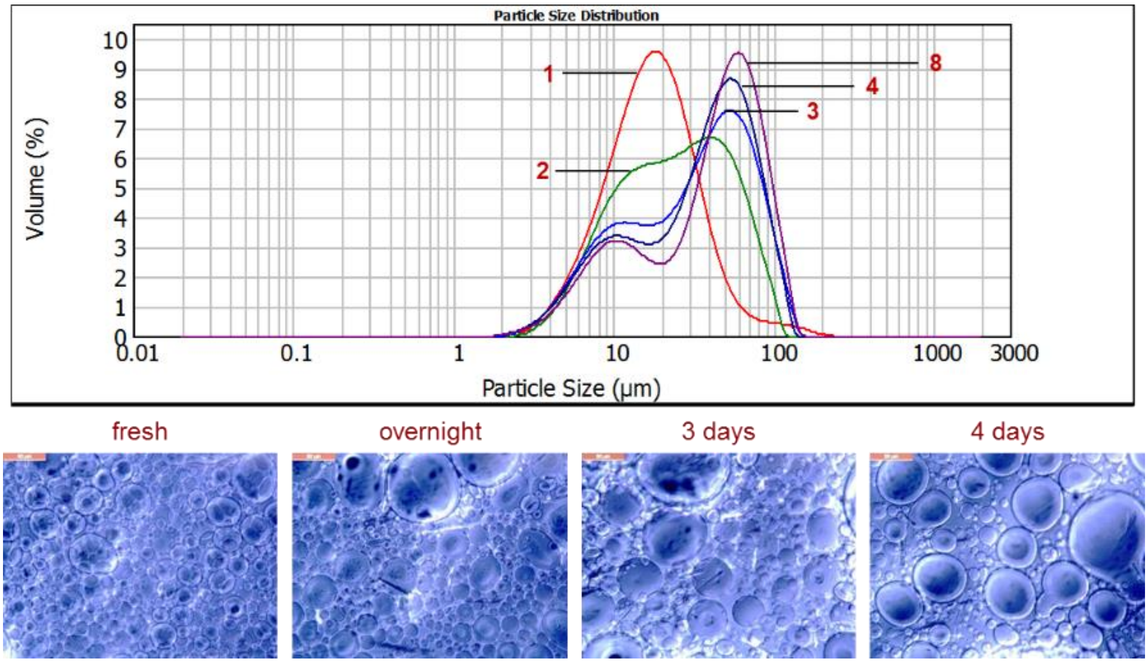


Figure 4.14: Droplet size distribution curves and respective microscopic images at various stages of ageing for the sample prepared using carboxylic acid POSS nanomolecules with Mosspar-H oil

After considering all the experimental findings of this investigation, it can be concluded that maleamic acid-isobutyl POSS nanomolecules do have a certain low capacity towards the formation and stabilisation of highly concentrated emulsions. However, due to the behaviour of these molecules within the oil phase, any further pursuance was rendered impossible. A detailed investigation of observed gelation phenomena falls outside the scope of current work since it requires a detailed focus around the processes and interactions of this particular type of nanomolecules and the other components of the system, with an investigation of the effects of various parameters within the system on these interactions in an attempt to fully understand the causes of such a phenomena as well as possible ways to overcome it or ultimately utilise it for the target purposes. It is important to note, however, that even though such a focused and in depth investigation of such phenomena was not intended in the current study, the phenomena was examined in closer detail and these results have been presented and discussed in previous sections.

4.3.4 Imide POSS nanomolecules

Molecular structure of the compound considered in this sub section is demonstrated in Figure 4.15. These molecules contain the imide functional group in their structure as well as i-butyl

R-group and have a molecular formula $C_{35}H_{71}NO_{14}Si_8$ with the name POSS maleimide isobutyl (IM0673).

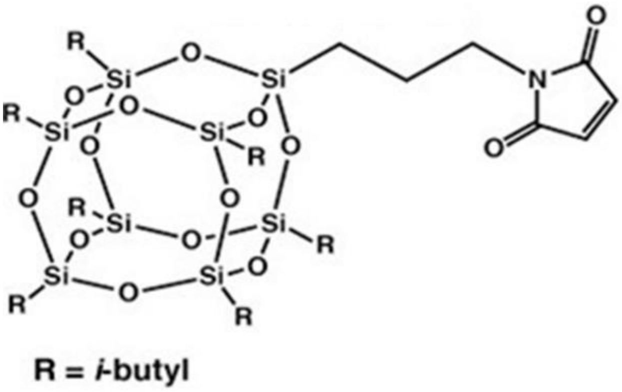


Figure 4.15: POSS maleimide isobutyl molecular structure

A summary of experimental results obtained is illustrated in Figure 4.16. Emulsion formation was possible for all the oils considered within the framework of current study.

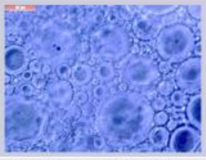
Oil	Emulsion	Inversion Point (%wt)	Stability	Microscopy
Mosspar - H		None. Target dispersed phase concentration of 90%wt is reached.	Immediate significant coalescence Separation – 2 days	
Ash - H		89.3	Significant coalescence – 8 days Separation – 10 days	
Parprol		72.8	Immediate significant coalescence Separation - overnight	Impossible to obtain. Emulsion breaks down to water and oil under shear.
Dodecane		89.6	Immediate significant coalescence Separation - overnight	Impossible to obtain. Emulsion breaks down to water and oil under shear.

Figure 4.16: Overview of the data obtained for the samples prepared using Maleamic acid-isobutyl POSS molecules

As can be seen from Figure 4.16, for low viscosity and low aromatic content Mosspar-H oil, the target aqueous phase concentration of 90% by weight has been successfully reached. Resultant emulsion demonstrated immediate significant coalescence on preparation with complete phase separation after two days from preparation. Coalescence on preparation was evident from the droplet size distribution curve for the sample demonstrated in Figure 4.17. The average droplet size within the sample was in the region of 100 microns. Microscopic observations were possible only for the freshly prepared sample due to instability under shear.

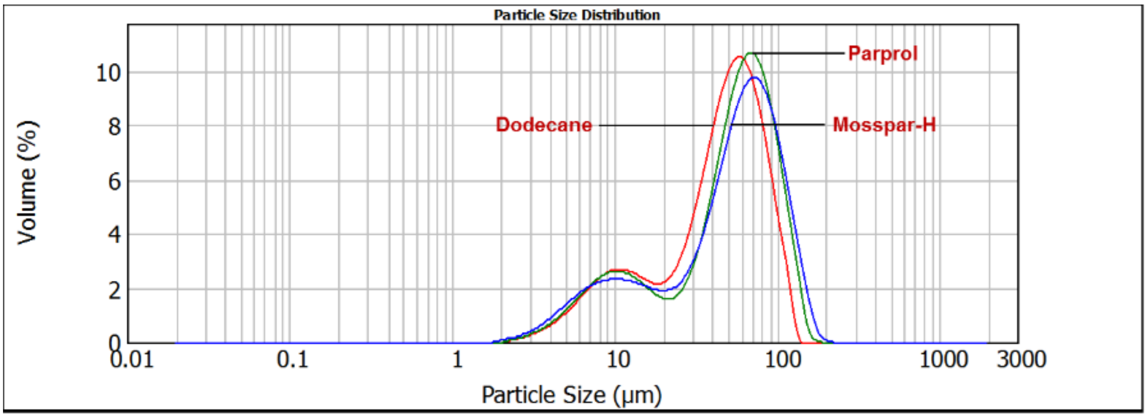
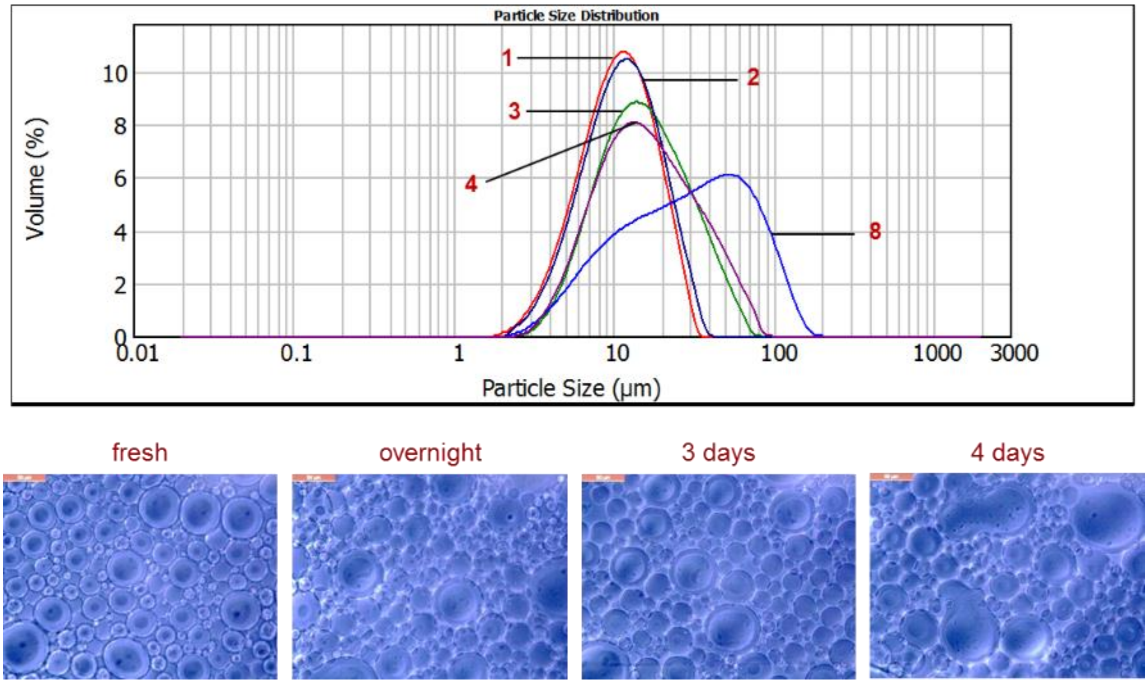


Figure 4.17: Droplet size distribution curves for the samples prepared using imide POSS nanomolecules with Mosspar-H, Parprol and Dodecane

For the highly viscous and high aromatic content, Parprol oil and laboratory grade Dodecane inversion points occurred at 72.8% and 89.6% respectively. Both of the resultant samples demonstrated high instability in terms of both significant coalescence straight after preparation and instability under shear, resulting in phase separation which rendered microscopic analysis of these samples impossible. Coalescence of fresh samples was evident from the droplet size distribution analysis, and resultant curves are presented in Figure 4.17. For both samples, the average droplet size was in the region of 100 microns. Moreover, both emulsions underwent full phase separation overnight.

For the sample prepared using low viscous Ash-H oil with high aromatic content as part of an oil phase, an inversion point occurred at the aqueous phase concentration of 89.3% by weight. This emulsion demonstrated a moderate stability throughout the first four days of observation, with rapid decrease by Day 8. This was evident from both the droplet distribution and microscopic investigations (Figure 4.18).

It can be seen from the droplet size distribution curves that resultant emulsions stayed stable the first two days of ageing with the first signs of coalescence apparent by Day 3. At Day 4, a moderate increase of coalescence was observed. This pattern was in full agreement with the microscope instigation of emulsion. By Day 8 of the investigation, a significant increase in coalescence within the sample was observed.



fresh

overnight

3 days

4 days

Figure 4.18: Droplet size distribution curves and respective microscopic images at various stages of ageing for the sample prepared using carboxylic acid POSS nanomolecules with Mosspar-H oil

At this point, emulsion became too unstable under shear for further microscopic investigation. A complete phase separation within the sample took place by Day 10 of the investigation. From the data obtained as a result of this experimental investigation, it is apparent that POSS maleimide isobutyl does have a capacity for the formation of highly concentrated emulsions. All the samples were successfully formed across the matrix of various oils with different properties, including pure laboratory grade Dodecane. However, emulsions prepared using low viscosity with low aromatic content Mosspar-H oil, highly viscous with high aromatic content Parprol and laboratory grade Dodecane, have all demonstrated very low stability for both coalescence and shear. For all of these samples, a complete structure degradation has been observed within two days of preparation. For emulsion prepared using low viscous and high aromatic content Ash-H oil, a moderate stability to both coalescence and under shear has been observed, which is especially evident as compared to the rest of the samples within the analysed set. This sample remained fairly stable throughout the first four days of investigation, with significant coalescence observed by Day 8 and full phase separation taking place by Day 10 of the investigation. Consequently, it can be concluded that imide POSS nanomolecules have the highest reactivity within the system of interest when contained in the low viscous highly aromatic media. Change in viscosity or aromatic content results in immediate drastic decrease of both the stability to coalescence and shear.

4.3.5 Amine POSS nanomolecules

In the scope of this investigation, a group consisting of three different types of amine POSS nanomolecules has been considered, as is necessary for gaining a better understanding of the influence of reactivity of a functional group, as well as the length of the hydrocarbon chain of the R-group of the molecules, on the ability of POSS molecules towards the stabilisation of the system under investigation, as well as the resultant overall stability of the highly concentrated emulsion. Figure 4.19 illustrates the molecular structure, along with the formula and chemical name, of the molecules under consideration. Additionally, it schematically illustrates the differences and similarities of the various functional groups within these molecules. Aminopropylisobutyl (AM0265) and aminopropylisooctyl (AM0270) POSS molecules both contain identical functional groups with terminal low reactive primary amine. On the other hand, these two molecules differ in the R-group hydrocarbon chain length, with AM0265 containing a shorter chain i-butyl group and AM0270 longer chain i-octyl.

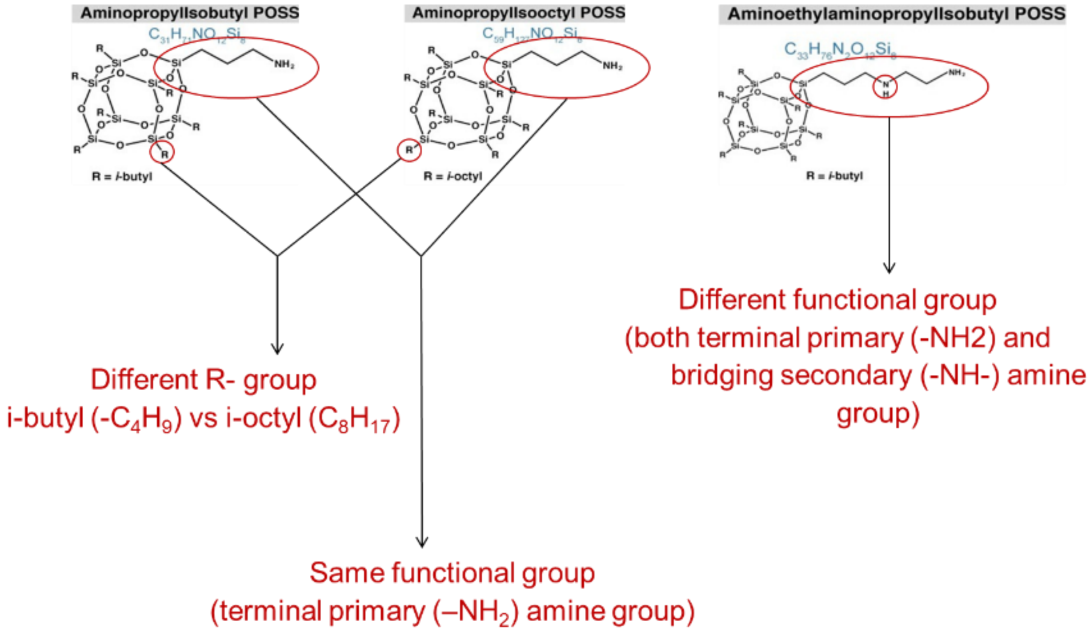


Figure 4.19: Molecular structures, chemical formulas, names and schematic comparison of aminopropylisobutyl (AM0265), aminopropylisooctyl (AM0270) and aminoethylaminopropylisobutyl (AM0275) POSS nanomolecules

It is important to mention that among other factors investigated and discussed in other sections, the length of the R-group contained within the molecule affects the resultant physical state that the compound exists in at ambient conditions. All the nanomolecules within the scope of the current investigation contained short chain i-butyl, yet another reason behind the addition of the aminoproptlisooctyl POSS to the matrix. Unlike all the other types of molecules under investigation that exist in the form of a fine solid powder, AM0270 is a viscous liquid under ambient conditions. At the same time, identical in every aspect except of R-group chain length, AM0265 exists, similar to all the other POSS molecules containing i-butyl group, in the form of fine white solid powder.

Aminoethylaminopropylisobutyl POSS molecules, as compared to the other two types of amine POSS nanomolecules within the group, contain a different functional group within their structure. As can be determined from the molecular structure of these molecules, the functional group contains both terminal low reactive primary amine group, similar to the other two types considered, as well a reactive bridging secondary amine group and an overall longer chain functional group. Furthermore, these molecules contain a short chain i-butyl R-group and hence exist in the form of fine solid powder, similar to aminopropylisobutyl POSS. Considering these types of nanomolecules allowed for a better understanding of the influence of reactivity of the functional group on both the ability towards the stabilisation of the highly concentrated emulsion and the effect on the overall stability of the final system.

The results obtained from experiments conducted with above mentioned molecules will be discussed separately as per the layout established in the previous sections.

4.3.5.1 Aminopropylisobutyl POSS

We first look at the aminopropylisobutyl (AM0265) POSS nanomolecules with the molecular formula $C_{31}H_{71}NO_{12}Si_8$. The molecular structure of this compound is demonstrated in Figure 4.20. These molecules contain an amine group as part of their functional group; in this particular case, in addition to the i-butyl R-group, a terminal primary amine is found.

A summary of experimental results obtained is illustrated in Figure 4.21. It was possible to form emulsions with all of the oils used in the investigation as part of the continuous phase. As can be seen from the presentation of results, for both of the low viscous oils Mosspar-H and Ash-H, an inversion point occurred at the aqueous phase concentration of 84% by weight within the system.

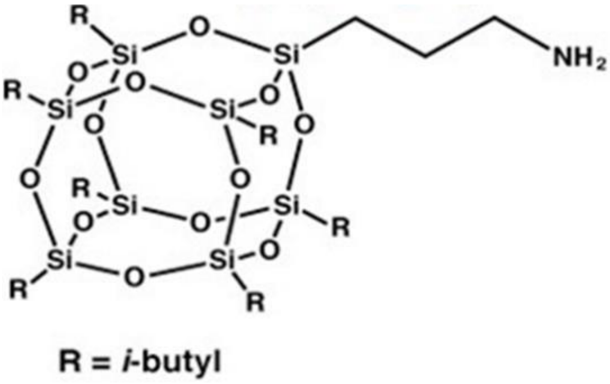


Figure 4.20: Aminopropylisobutyl POSS molecular structure

Low aromatic content Mosspar-H oil has demonstrated a stability of 12 days with significant coalescence that occurred by Day 16 of ageing. On the other hand, for the high aromatic content Ash-H oil, the resultant system demonstrated a mere one day stability with significant coalescence by Day 2 of the investigation.

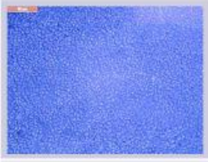
Oil	Emulsion	Inversion Point (%wt)	Stability	Microscopy
Mosspar - H		84	12 days Significant coalescence - 16 days	
Ash - H		84	Significant coalescence – 3 days Separation – 8 days	
Parprol		77.7	>50 days (slow progressing coalescence)	
Dodecane		88	Immediate significant coalescence Separation – overnight	Impossible to obtain. Emulsion breaks down to water and oil under shear.

Figure 4.21: Overview of the data obtained for the samples prepared using Aminopropylisobutyl POSS molecules

Emulsion prepared using laboratory grade Dodecane as a medium for the oil phase demonstrated an inversion point at 88% concentration by weight of ammonium nitrate. This system was highly unstable, with immediate significant coalescence taking place upon sample preparation.

Coalescence was clearly evident from droplet size distribution analysis; the resultant curve is presented in Figure 4.22. A complete degradation of the sample in the form of phase separation occurred overnight. Microscopic analysis of the sample was impossible due to extreme instability under shear resulting in phase separation during the microscopic slide preparation.

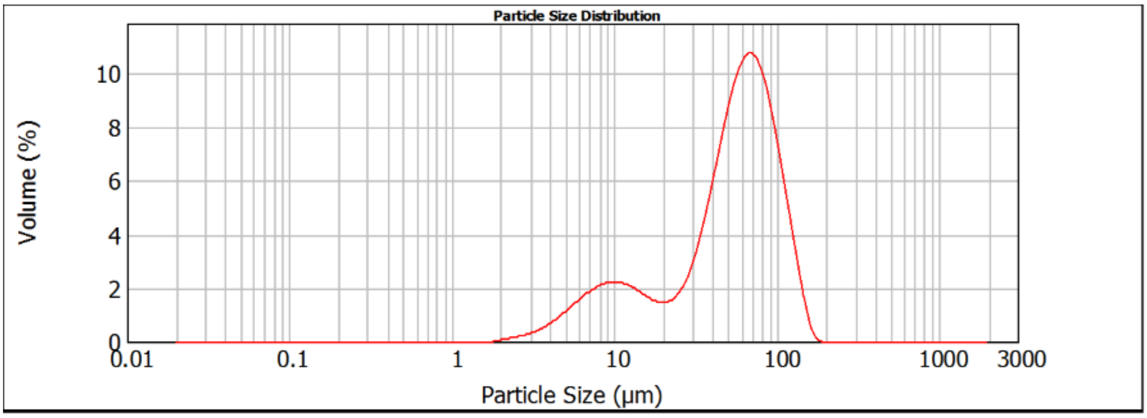


Figure 4.22: Droplet size distribution curves for the samples prepared using amine (AM0265) POSS nanomolecules with laboratory grade Dodecane

Figure 4.23 presents the results of both droplet size and microscopic investigation of the sample prepared with low viscosity and low aromatic content Mosspar-H oil. As can be seen from droplet size distribution curves, the sample remained fairly stable through the first four days of ageing, with an insignificant overall peak shift occurring towards the region of larger droplet size. By Day 8 of investigation, however, a broadening of the peak was observed as compared to previous measurements which indicated progressing coalescence. This broadening increased by Day 12 of the ageing of the system. By Day 16, a distinguished shift of the peak towards the region of large droplet size was observed. Finally, at Day 24, the majority of droplet sizes within the system reached the region of 100 microns.

The droplet size distribution investigation was accompanied by microscopic observations and the two were in full agreement throughout the period of possible observations. Microscopy of the system was possible to obtain only during the first eight days of ageing; thereafter the system became too unstable under shear, rendering microscopic slide preparation impossible due to phase separation.

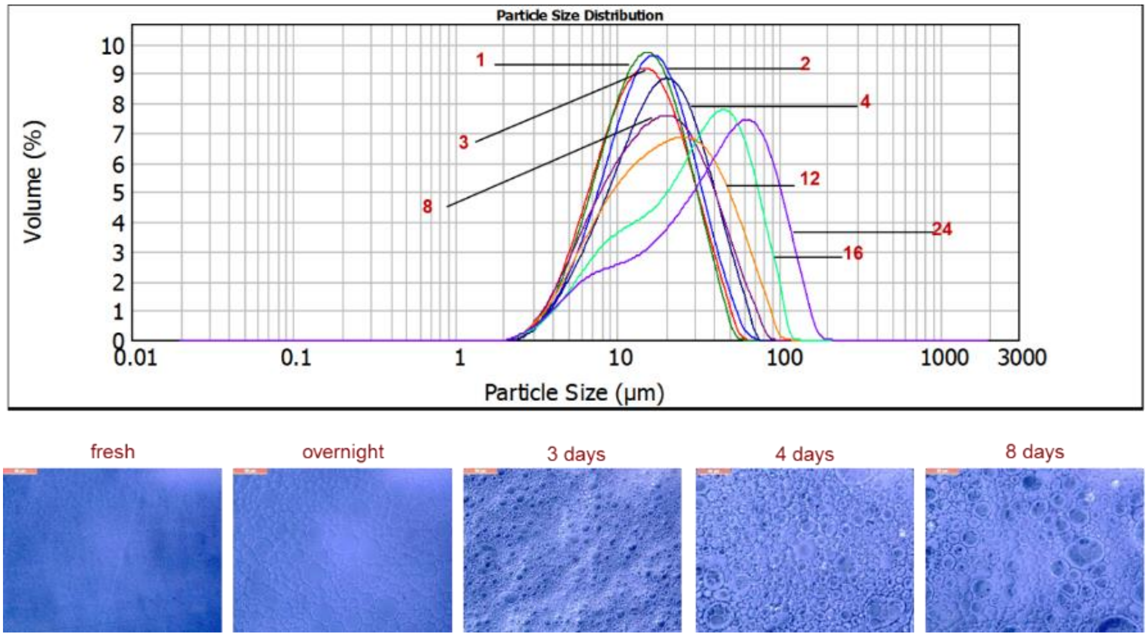


Figure 4.23: Droplet size distribution curves and respective microscopic images at various stages of ageing for the sample prepared using amine (AM0265) POSS nanomolecules with Mosspar-H oil

Droplet size distribution curves and microscopic pictures for the sample prepared with low viscosity and high aromatic content Ash-H oil are demonstrated in Figure 4.24.

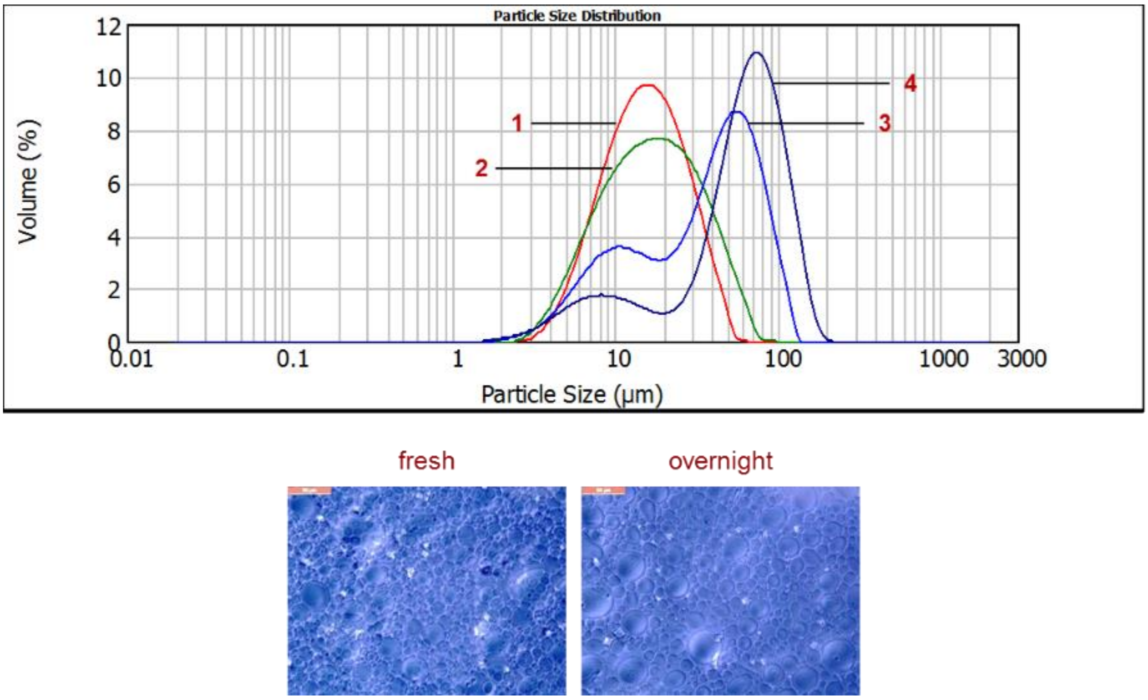


Figure 4.24: Droplet size distribution curves and respective microscopic images at various stages of ageing for the sample prepared using amine (AM0265) POSS nanomolecules with Ash-H oil

Immediately on preparation, the droplet size analysis indicated a wide distribution. Further coalescence was observed the following day. By Day 3 of observations, a complete shift of the droplet size into the region of 100 microns took place with further drastic increase by Day 4.

Microscopic observations were possible for the first two days after emulsion preparation, past which system became highly unstable under shear and any attempt of microscopic slide preparation resulted in phase separation on the microscopic slide. The first two days of microscopic observations are in full agreement with the data obtained from the droplet size distribution investigation; coalescence was observed in the fresh sample and increased overnight. Additionally, microscopic data illustrated further destabilisation of the system in the form of minor crystallisation. Full degradation of the sample in the form of complete phase separation took place by Day 6 of the investigation.

The highest stability of the system prepared with the use of aminopropylisobutyl POSS molecules has been achieved in the highly viscous and aromatic content media of Parprol oil.

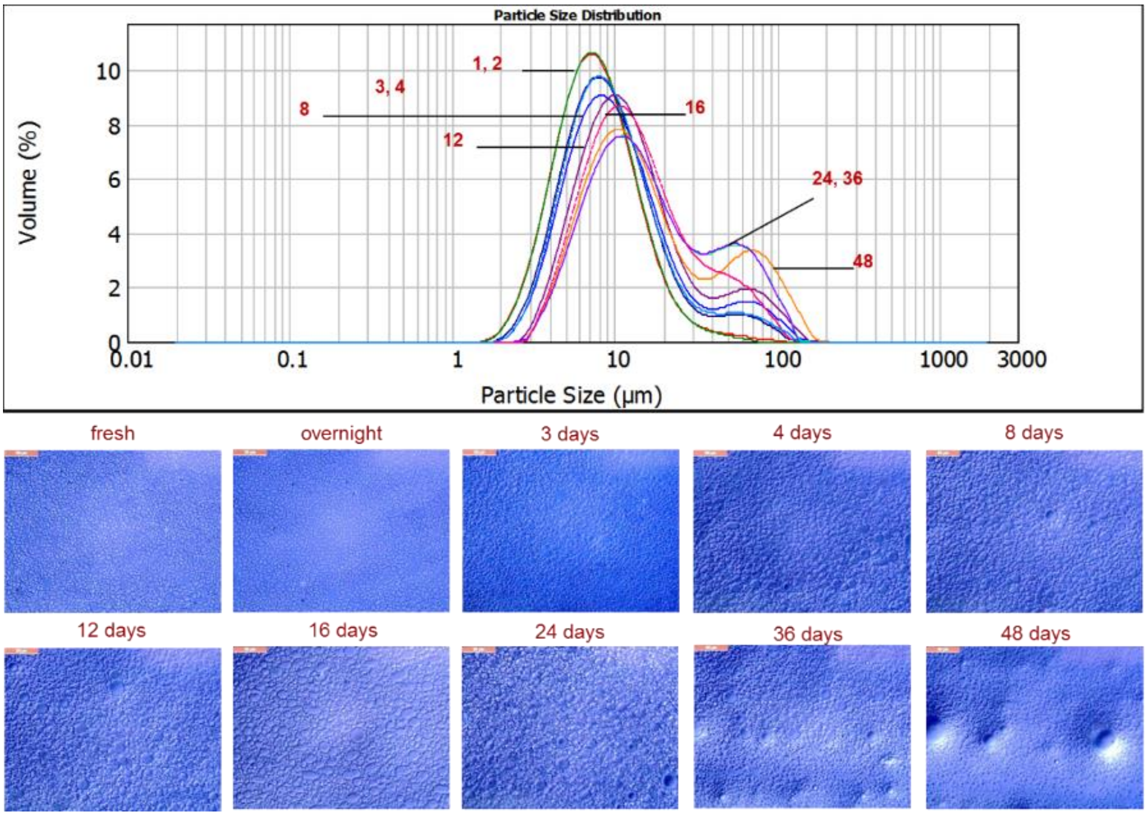


Figure 4.25: Droplet size distribution curves and respective microscopic images at various stages of ageing for the sample prepared using amine (AM0265) POSS nanomolecules with Parprol oil

The inversion point for this sample occurred at 77.7% by weight of ammonium nitrate within the system. The resultant sample demonstrated moderate stability of over 50 days with slow progressing coalescence. Figure 4.25 illustrates experimental results of the droplet size distribution as well as microscopic observations of the system. Throughout the first two days after preparation, the system remained fairly stable, with no coalescence taking place and a very narrow droplet size distribution peaking at the approximate size of 10 microns. The first signs of coalescence were observed in the sample by Day 3 with a minor broadening and shift of the peak taking place. However, due to a very low rate of coalescence, no significant further degradations of the sample were observed at Day 4 of ageing as compared to Day 3. Further slow progressing distribution broadening with average droplet size increase was observed at Days 8, 12 and 16 of the investigation. By Day 24 of sample ageing, distinct separation of the droplet sizes contained within the system was observed, expressed by the occurrence of the second peak in the droplet size distribution curve in the region of 100 microns. It is important to note, however, that at this point of investigation the predominant majority of the droplets remained in the size of approximately 10 microns, an indication of minor overall coalescence taking place within the system at a very slow rate. No changes were observed in the system at Day 36 as compared to Day 24. By observation Day 48, the peak indicating the coalesced portion of the sample became more prominent; however, no significant changes were once again observed in the system.

Considering a fair stability of the observed system throughout the first 50 days of investigation, an unexpected rapid degradation of the sample took place shortly after this point of ageing with a complete phase separation by Day 60. The system reached a critical point of the amount of coalesced droplets within as compared to the ones remaining at the approximate of 10 micron which, in turn, catalysed destabilisation process resulting in escalation of coalescence rate, leading to rapid system integrity degradation.

Importantly, the system remained fully stable under shear through the entire investigation which allowed for full microscopic observations. The resultant microscopy was in full agreement with droplet size distribution analysis, with slow progressing coalescence observed from the day of preparation throughout to Day 48 of ageing. At the end stage of the observations, it was clear from microscopic photos that the sample contained two types of droplets, with larger ones being the minor portion, as per the droplet size distribution.

From the data collected throughout the experiment, then subsequently analysed and discussed, it can be concluded that aminopropylisobutyl POSS nanomolecules possess a proclivity for both the formation and stabilisation of highly concentrated emulsions. Successful emulsion formation was possible in all the oil media considered in the scope of this current study. The stability of the resultant sample, however, demonstrated a high dependency on the individual properties of the media. The best stability of over 50 days with slow progressing coalescence has been observed for the sample prepared using the highly viscous and high aromatic content Parprol oil. The rest of the samples showed a total stability varying from zero to 12 days with significant rapidly occurring coalescence of the droplets. These types of POSS molecules have demonstrated much better ability towards stabilisation of the system under consideration than the ones considered previously. Additionally, a fairly high ageing stability of the sample prepared with the use of Parprol oil may be explained by the fact that highly viscous oil assists in preserving the integrity of the system and retarding the rate of coalescence.

4.3.5.2 Aminopropylisooctyl POSS

We now consider aminopropylisooctyl (AM0270) POSS nanomolecules with the molecular formula $C_{59}H_{127}NO_{12}Si_8$. These nanomolecules are identical to aminopropylisobutyl (AM0265) in every way except the length of the R-group, with AM0270 containing long chain i-octyl against the shorter chain i-butyl in the case of AM0265 (Figure 4.26). It can be seen that both AM0265 and AM0275 indeed contain the same functional group with the terminal primary amine. It is important to note that AM0270 nanomolecules were the only type within the whole set investigated to contain the long hydrocarbon chain R-group; all the rest of the nanomolecules contained the shorter chain length i-butyl group.

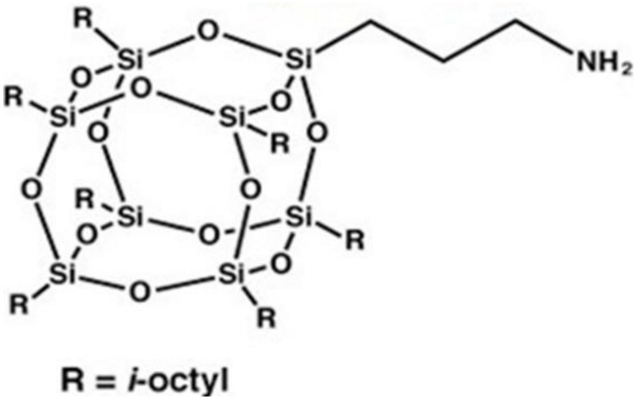
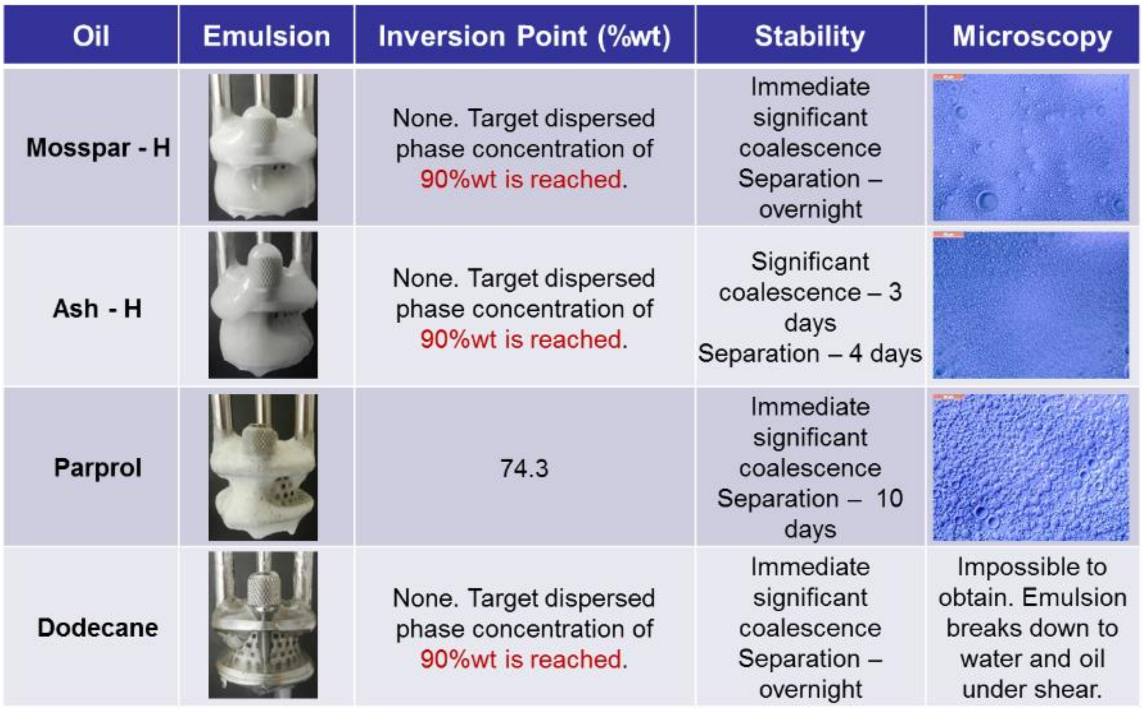


Figure 4.26: Aminopropylisooctyl POSS molecular structure

The approach of selecting two types of molecules related in every aspect except the R-group allowed us to successfully investigate and determine the effect of the R-group hydrocarbon chain length on the stability of the system under investigation and determine whether the shorter or the longer length chain is more favourable and suitable.

As opposed to all the previously considered nanomolecules that exist in the form of fine crystalline powder at the ambient conditions, aminopropylisooctyl POSS is the moderately viscous liquid. Since all the molecules, whilst containing completely different types of functional groups, possessed i-butyl as the R-group, the different aggregate state of AM0270 at ambient conditions may be fully attributed to the longer chain i-octyl R-group. This in itself was already an indication of potential impacts of the hydrocarbon chain length of the R-group contained within the molecules on both the ability towards the formation of the system as well as the long term ageing stability.

Figure 4.27 presents an overview of results obtained from experimental work performed with the use of aminopropylisooctyl POSS nanomolecules.



Oil	Emulsion	Inversion Point (%wt)	Stability	Microscopy
Mosspar - H		None. Target dispersed phase concentration of 90%wt is reached.	Immediate significant coalescence Separation – overnight	
Ash - H		None. Target dispersed phase concentration of 90%wt is reached.	Significant coalescence – 3 days Separation – 4 days	
Parprol		74.3	Immediate significant coalescence Separation – 10 days	
Dodecane		None. Target dispersed phase concentration of 90%wt is reached.	Immediate significant coalescence Separation – overnight	Impossible to obtain. Emulsion breaks down to water and oil under shear.

Figure 4.27: Overview of the data obtained for the samples prepared using Aminopropylisooctyl POSS molecules

Emulsion formation was possible with all of the oils used as part of the continuous phase within the scope of the current investigation. For three of the four oils considered, the Mosspa-H, Ash-H and laboratory grade Dodecane target dispersed phase concentration of 90% by weight within the system has been obtained. Consequently, no emulsion inversion took place. For highly viscous and high aromatic content Parprol oil, emulsion inversion occurred when the dispersed phase concentration within the system reached 74.3% by weight. As compared to the aminopropylisobutyl POSS nanomolecules, where target dispersed concentration was not reached with any of the oils used in preparation of emulsion, it was concluded that i-octyl R-group does contain an increased capacity towards the stabilisation of larger amounts of dispersed phase and hence successful formation of the system.

The sample that resulted from stabilisation of the system with AM0270 nanomolecules in the laboratory grade Dodecane demonstrated high instability. Immediate significant coalescence was observed. Moreover, the sample was too unstable under shear, rendering microscopic slide preparation and therefore analysis impossible. Emulsion phase separation of this sample took place the following day after preparation. The droplet size distribution curves demonstrating coalescence within the freshly prepared sample for both laboratory grade Dodecane and Mosspar-H oil are demonstrated in Figure 4.28.

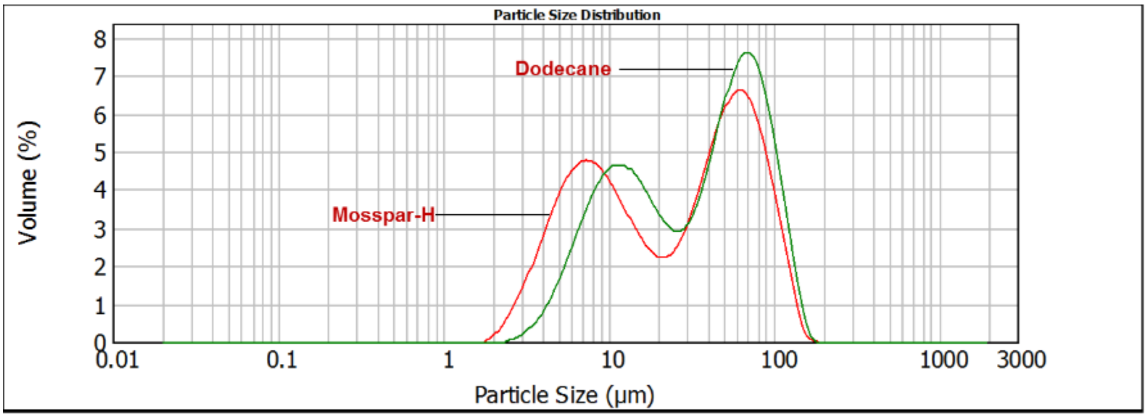


Figure 4.28: Droplet size distribution curves for the samples prepared using aminopropylisooctyl POSS nanomolecules with Mosspar-H and Dodecane

As can be deduced from the curves presented, similar results were obtained for the system stabilised with low viscous and low aromatic content Mosspar-H oil. However, in this case, the system was stable enough under shear to perform the microscopic analysis of the sample. Significant coalescence with phase separation overnight was observed.

A sample prepared using highly viscous and highly aromatic Parprol oil has demonstrated immediate moderate coalescence within the freshly prepared emulsion. The droplet size distribution analysis of this sample is presented in Figure 4.29. As revealed from the obtained results, the system demonstrated a rapidly increasing rate of coalescence. An increase of the number of droplets with a size in the region of 100 microns has been observed immediately from Day 1 of the investigation, onto Day 2 and further on until by Day 8 of observations, at which point the number of coalesced droplets exceeded the number with the average size in the 10 micron region. This has been confirmed by microscopic investigation until the sample was stable enough under shear. After Day 3 of the investigation, it became impossible to perform any further microscopic observations due to emulsion phase separation during the preparation of microscopic slides. The sample itself underwent complete degradation in the form of phase separation by Day 10 of ageing.

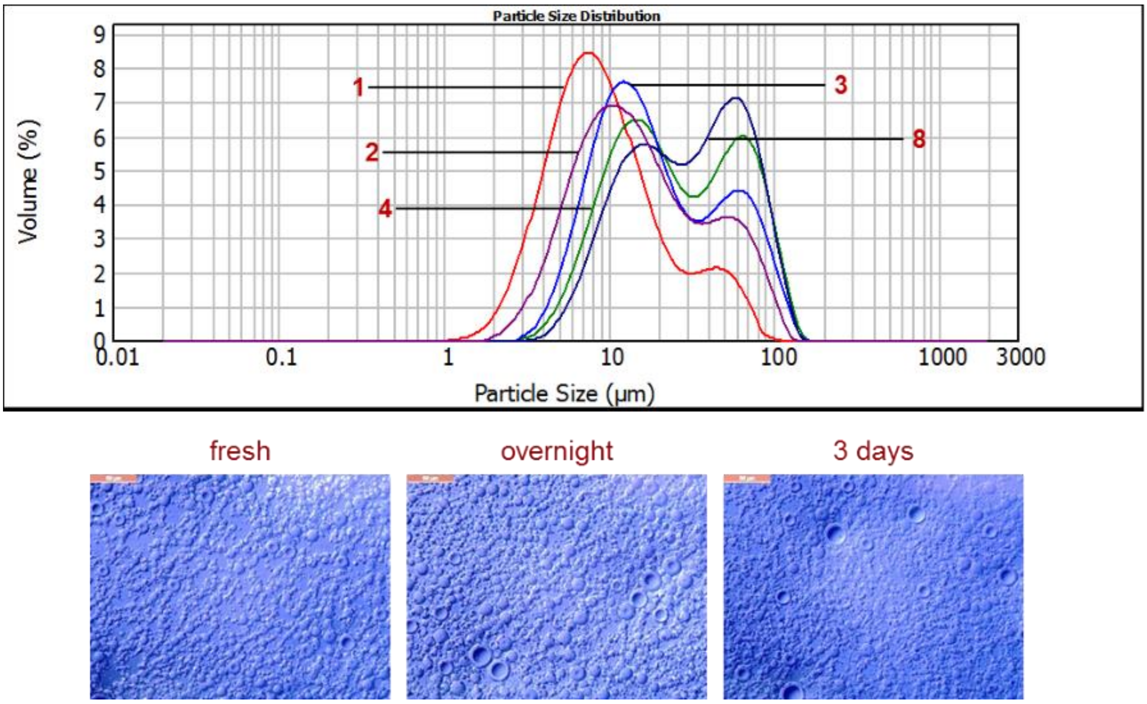


Figure 4.29: Droplet size distribution curves and respective microscopic images at various stages of ageing for the sample prepared using amine (AM0270) POSS nanomolecules with Parprol oil

Emulsion oil phase containing low viscous and high aromatic content Ash-H oil as media for dispersion of nanomolecules initially demonstrated good ability towards the stabilisation of the system on both preparation and throughout the first two days of ageing. However, after Day 2 of the investigation, a rapid substantial coalescence within the sample occurred. Droplet size distribution curves for this sample are presented in Figure 4.30. During the first two days of ageing, no changes within the sample were observed; however, analysis at Day 3 of ageing revealed a substantial shift of average droplet size into the 100 micron region accompanied by a widening of the droplet size distribution. Microscopic investigation of the sample was possible only at Day 1 and 2 and by Day 3 the system became too unstable under shear with any attempts of microscopic slide preparation resulting in emulsion phase separation. Moreover, microscopy taken at Day 2 of ageing already revealed destabilisation of the sample under shear. This can be seen in the photo in the form of individual large droplets within the otherwise uniform sample. The sample underwent complete phase separation by Day 4 of ageing.

Experimentally obtained data demonstrated the ability of the aminopropylisooctyl POSS nanomolecules towards the stabilisation of high amounts of dispersed phase within the system as compared to aminopropylisobutyl and other nanomolecules considered previously in this investigation. The target dispersed phase concentration was reached with three of the four oils considered within the scope of this current study.

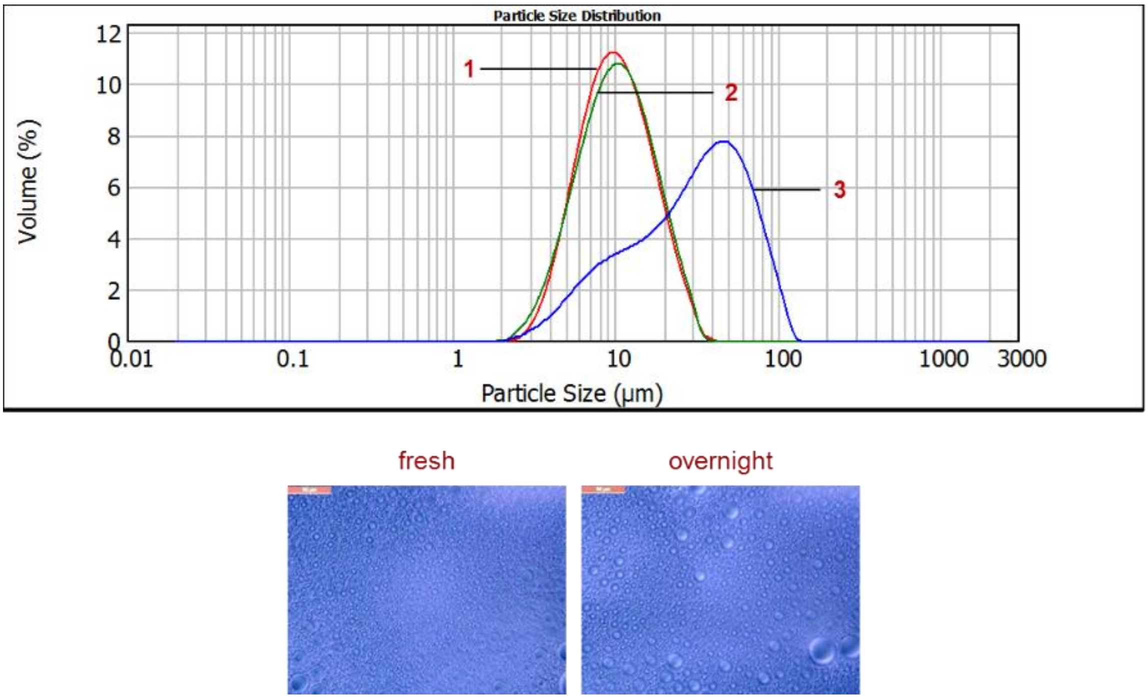


Figure 4.30: Droplet size distribution curves and respective microscopic images at various stages of ageing for the sample prepared using amine (AM0270) POSS nanomolecules with Ash-H oil

Nevertheless, despite an increased ability towards tolerance of higher amounts of dispersed phase, detailed analysis and discussion of experimental results revealed a very low capacity of AM0270 nanomolecules for providing the stability of the resultant system on shelf. Samples prepared using laboratory grade Dodecane and Mosspar-H oil have both reached the target dispersed phase concentration during preparation. However, the resultant systems in both cases have demonstrated significant coalescence with subsequent overnight full structure degradation in the form of emulsion phase separation. For Parprol oil, immediate destabilisation of the system on preparation was observed with fast progressing coalescence; the resultant sample underwent phase separation by Day 10 of the investigation. This can be attributed to the high viscosity of the oil media which in itself preserved the integrity of the system as compared to the low viscous oils. Finally, low viscosity and high aromatic content Ash-H, similar to other investigated oils, resulted in the sample of low stability. In this case, however, the sample remained unchanged within the first two days of the investigation, with rapid coalescence occurring between Days 2 and 3. By Day 4, the system underwent a complete degradation.

Overall, identical in every aspect except of R-group aminopropylisobutyl POSS nanomolecules, the presence of the long hydrocarbon chain R-octyl group in the molecules resulted in the significant decrease in ability of the molecules towards the stabilisation of the system, both on the shelf and under shear. This can be attributed to the steric hindrance between the individual POSS nanomolecules that arises as a result of the long chain R-group, both at the interface between the phases of the system and within the continuous phase. This steric hindrance effectively leads to the overall drastic destabilisation of the final system.

4.3.5.3 Aminoethylaminopropylisobutyl POSS

The final type of POSS nanomolecules that has been investigated in the current study was aminoethylaminopropylisobutyl (AM0275) POSS. These molecules contain the functional group with both a more reactive bridging secondary amine as well as the terminal primary amine. The R-group within the molecule is a short hydrocarbon chain i-butyl, similar to aminopropylisobutyl, as discussed previously. The chemical formula of this compound, $C_{33}H_{76}N_2O_{12}Si_8$, and the chemical structure, are presented in Figure 4.31. It is important to note that the addition of these molecules into the system resulted in the gelation phenomenon occurring at the interface between the phases (see Figures 4.1 and 4.4). This gelation is independent of the type and properties of oil used as a media. The formed interfacial barrier is stable and rigid, allowing for complete encapsulation of the ammonium nitrate solution within (as illustrated in Figures 4.2 and 4.3). It has also been demonstrated that this gelation occurs *only* at the area of contact between the phases, and dispersed phase beyond the formed boundary remains in the uncompromised state. This was demonstrated by sucking the dispersed phase solution out of the gel pocket formed. Performed within the continuous phase using the nozzle that introduced the dispersed phase in, after the disperse phase was sucked out, it effectively left an empty gel shell (Figure 4.4). This further illustrates the rigidity of the formed interfacial film.

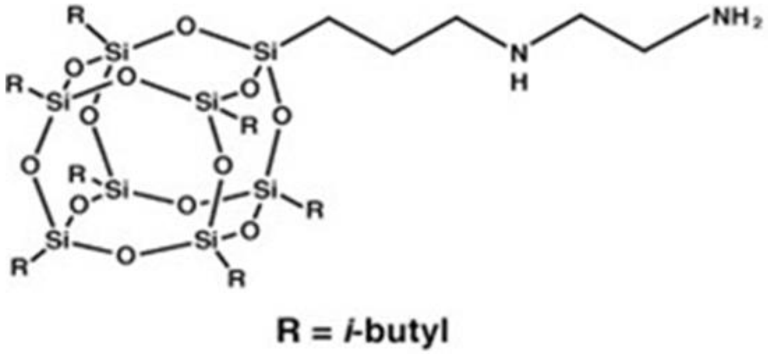


Figure 4.31: Aminoethylaminopropylisobutyl POSS molecular structure

An overview of experimentally obtained results is presented in Figure 4.32. Successive emulsion formation occurred with all of the oils considered in the current investigation.

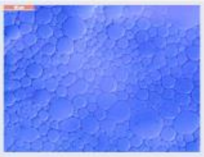
Oil	Emulsion	Inversion Point (%wt)	Stability	Microscopy
Mosspar - H		83.5	>200 days	
Ash - H		84	>100 days	
Parprol		75.1	Stable for >50 (moderate progressing coalescence)	
Dodecane		87.9	Stable for >50 (slow progressing coalescence)	

Figure 4.32: Overview of the data obtained for the samples prepared using Aminoethylaminopropylisobutyl POSS molecules

It is important to note that for these nanomolecules, no emulsion phase inversion took place. An inversion point term is kept for consistency; however, in this section it refers to the point at which the system simply stopped accepting any further amount of dispersed phase.

Sample prepared using low viscous and low aromatic content Mosspar-H oil stopped accepting ammonium nitrate solution at the total amount of 83.5% by weight within the system. The resultant system demonstrated an exceptional stability. Both droplet size distribution and microscopic analysis results are presented in Figure 4.33.

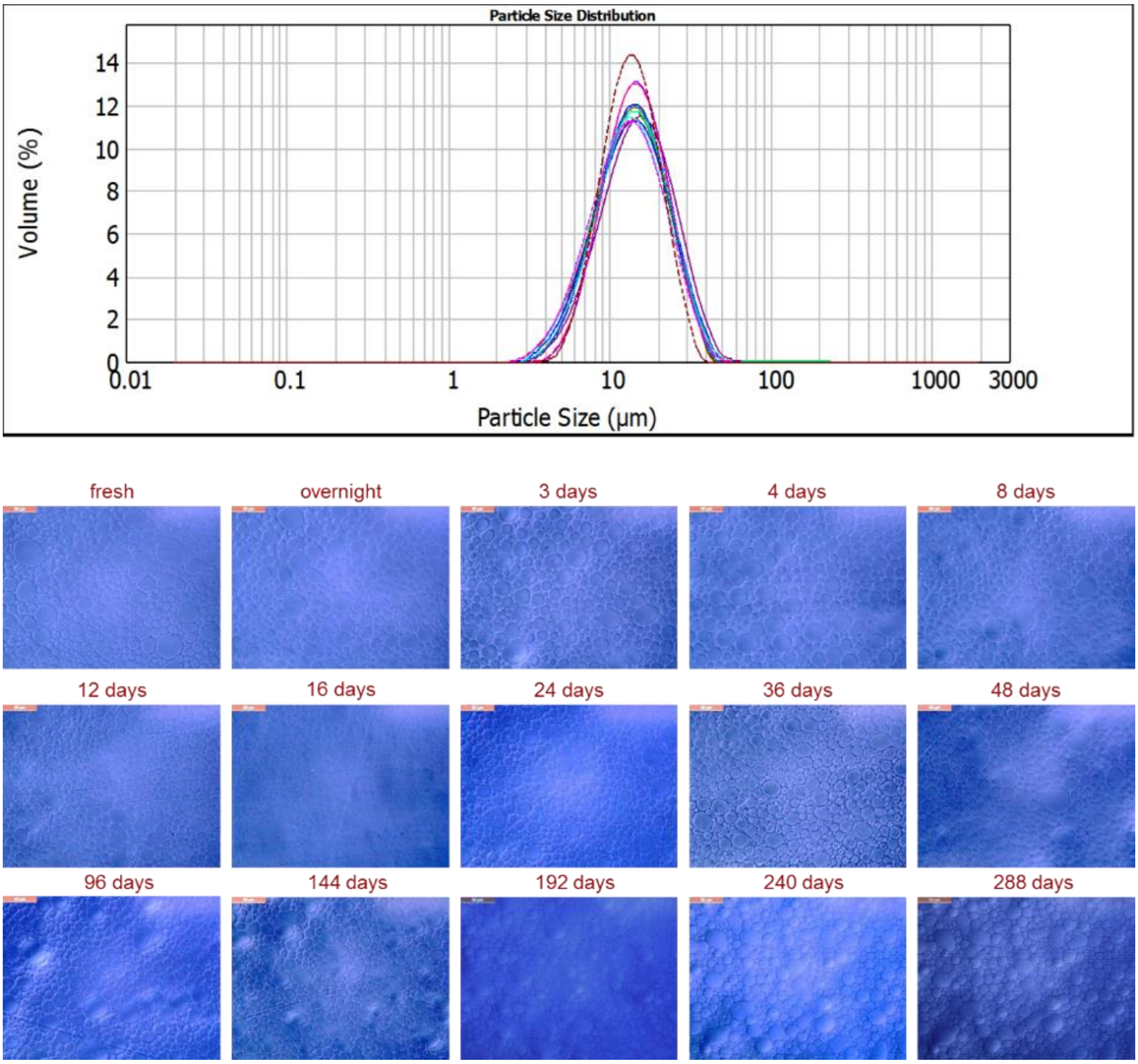


Figure 4.33: Droplet size distribution curves and respective microscopic images at various stages of ageing for the sample prepared using amine (AM0275) POSS nanomolecules with Mosspar-H oil

The sample was observed for a total of 288 days, throughout which period no structure changes or notable destabilisation of the system occurred. As seen from droplet size curves, no distribution peak shift or curve broadening was observed.

The insignificant difference in widths of the individual curves is a normal variation in measurements: no two measurements yield identical results. Therefore, this was not an indication of destabilisation of the system. Results of droplet size distribution investigation were fully supported by the microscopic analysis.

It was observed that from Day 1 of emulsion preparation until Day 288, no significant coalescence took place within the structure of the sample. It is important to emphasise that microscopic analysis was possible to perform throughout the entire period of sample observation, indicating the high stability of the sample under shear that additionally remained during ageing. Only slight destabilisation under shear was observed at Day 240 and Day 288 of ageing. This is indicated by a partial slight increase in droplet size on the microscopic photographs. Since droplet size distribution analysis confirmed no coalescence occurring within the structure of the sample, the slight increase of droplet size was attributed completely to the insignificant under shear stability decrease. It is important to note that the system under consideration remained stable past the Day 288 investigation point presented in the current discussion; however, no further analysis results were available at the point of presenting this study. In addition, the results clearly illustrate an exceptional stability both to coalescence and under shear of the said system and hence any results obtained from further investigation would once again support this finding and would not bare any crucial value.

The systems stabilised with the use of AM0275 POSS molecules and low viscosity with high aromatic content Ash-H oil stopped accepting dispersed phase when the total concentration in the sample reached 84% by weight. This is similar to the result obtained when continuous phase comprised low viscosity and low aromatic content oil. The resultant sample demonstrated an above average stability. The system remained completely stable and free from coalescence until Day 96 of observation. The same was true for stability under shear: results of both droplet size distribution and microscopic investigations of the sample are presented in Figure 4.34.

Droplet size curve peak shift was observed at Day 144 of ageing. This was not a significant change; however, it was considerable enough and could not be attributed to the uncertainty within measurements. At this point of observations based solely on the droplet size distribution within the sample, no significant changes occurred from which to draw conclusions and stop the investigation. However, microscopic analysis of the system revealed destabilisation in the form of dispersed phase crystallisation occurring in the system. Crystallisation in the sample causes uncertainty in the droplet size distribution measurements since it gradually becomes impossible to distinguish between coalescence and crystallisation within the specimen and thereby attribute the nature of the peak shift or occurrence of the secondary peak to either phenomenon. Additionally, in general, occurrence of crystallisation in the system is accompanied by droplet coalescence, or alternatively, droplet coalescence effectively leads to droplet crystallisation.

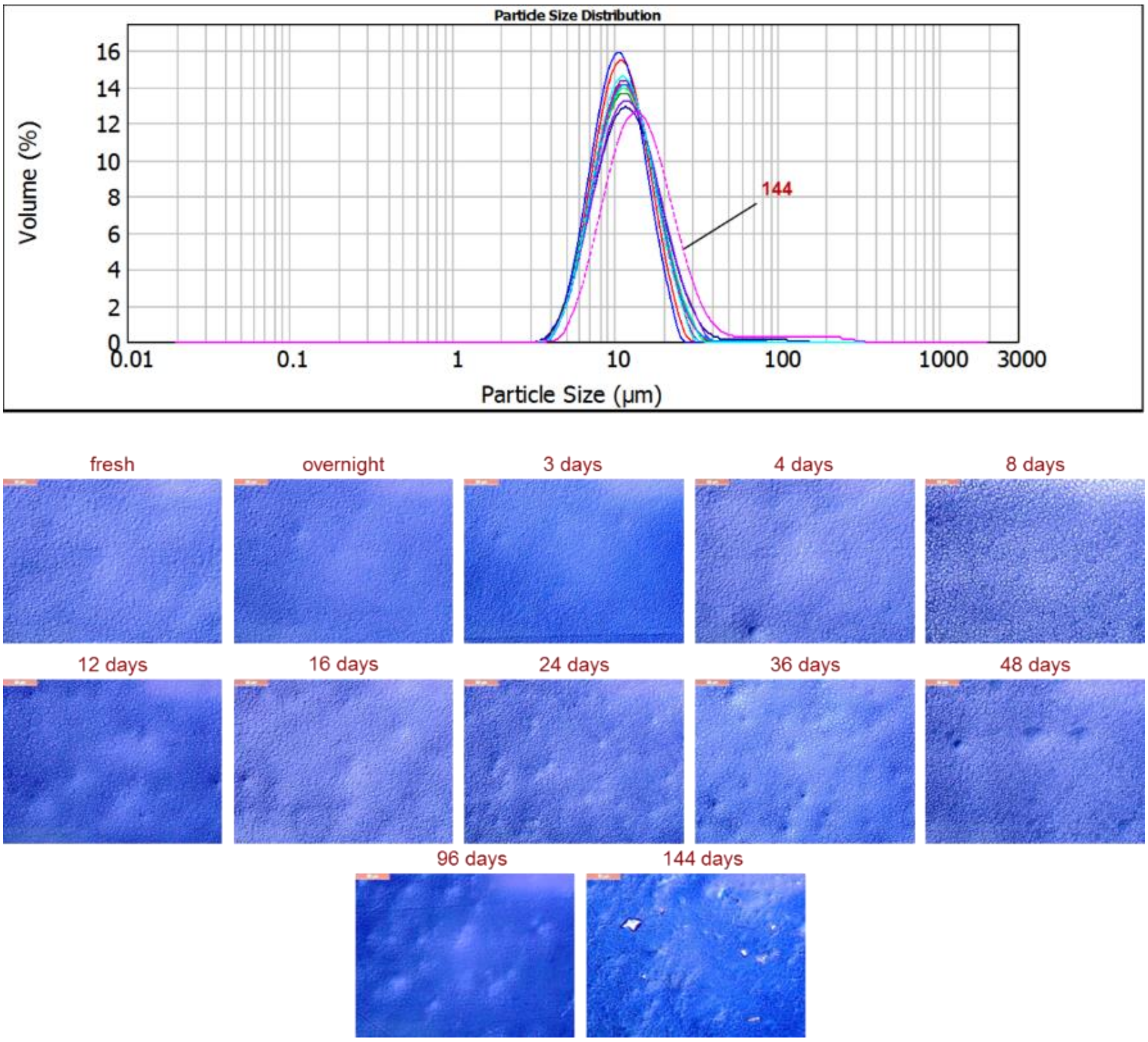


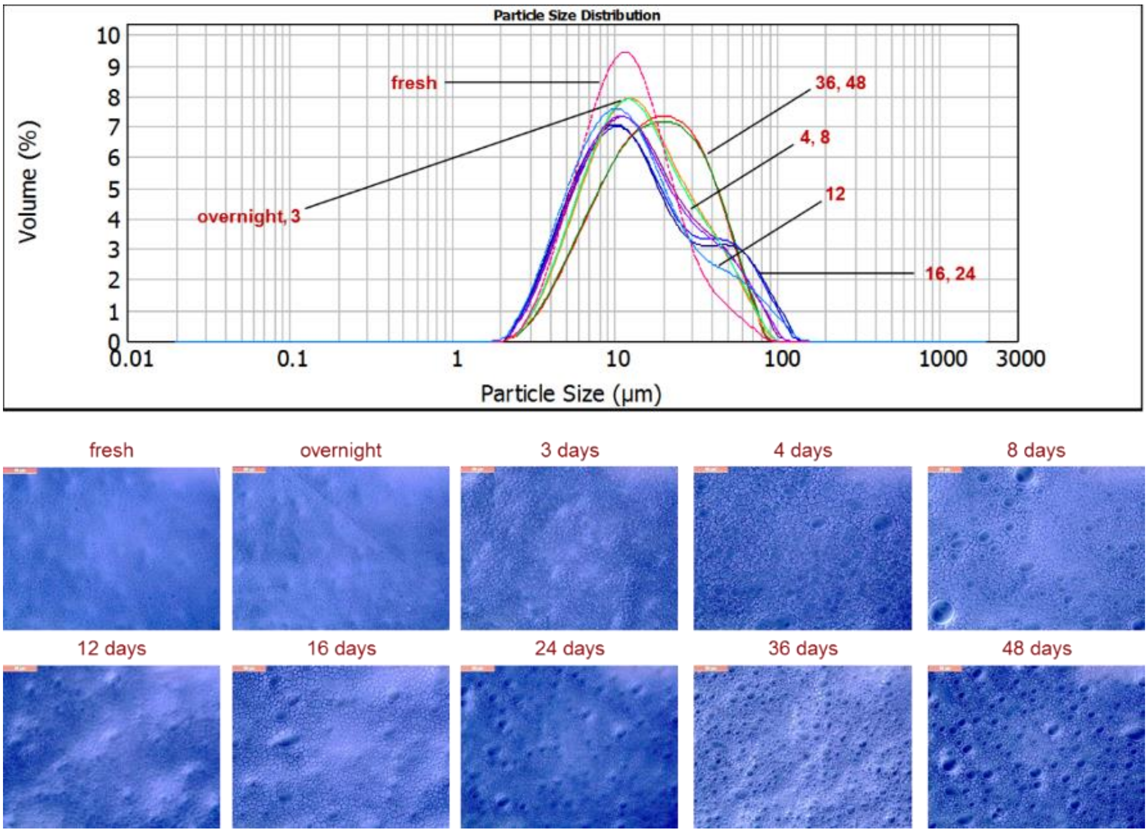
Figure 4.34: Droplet size distribution curves and respective microscopic images at various stages of ageing for the sample prepared using amine (AM0275) POSS nanomolecules with Ash-H oil

So, unless cases are exceptional, crystallisation does not occur without prior and simultaneous coalescence taking place in the system. Therefore, the resultant changes in the droplet size distribution curves, generally reflect both destabilisation effects simultaneously.

Due to the above, no further investigation was performed after Day 144 of ageing of the sample. Under shear stability accessed by microscopic investigation was in agreement with the droplet size distribution analysis. Minor destabilisation of the system under shear was observed after Day 9 of the investigation in the form of partially increased droplet size. The number of the droplets that were larger in size, as compared to the bulk of the sample, increased with ageing of the system, attributable to the decrease of system stability under shear since droplet size distribution analysis at respective times did not indicate any coalescence. Results obtained have illustrated most notably that the aromatic content of the oil used as a media for dispersion of POSS nanomolecules has a major impact on the stability of the system, both to coalescence and under shear.

Higher aromatic content of the media resulted in lower overall stability. Consequently, these types of oils are unavoidable for use with nanomolecules under discussion when the goal is to achieve the best overall stability of the system of interest.

Experimental results of the droplet size distribution, analysis as well as the microscopic investigation of the emulsion stabilised using aminoethylaminopropylisobutyl POSS nanomolecules, dissolved in the highly viscous with high aromatic content Parprol oil, are illustrated in Figure 4.35. This sample stopped accepting ammonium nitrate solution as soon as the dispersed phase concentration reached 75.1% by total weight. The stability demonstrated by the resultant system was over 50 days; however, a moderate rate of coalescence was observed throughout the entire period of observation. The system did not show any signs of coalescence fresh on preparation; but after an overnight analysis peak, broadening was already observed. This further progressed throughout until Day 8 of ageing. At Day 12 of the investigation, the first signs of secondary peak occurring closer to the droplet size region of 100 micron were observed, and by Day 16, this became prominent, remaining until Day 24 of the investigation. Analysis of the sample performed at Day 36 of ageing revealed both drastic broadening of the overall droplet size distribution curve as well as a complete shift of the peak into the region of the larger droplet size.



fresh
overnight
3 days
4 days
8 days
12 days
16 days
24 days
36 days
48 days

Figure 4.35: Droplet size distribution curves and respective microscopic images at various stages of ageing for the sample prepared using amine (AM0275) POSS nanomolecules with Parprol oil

This remained unchanged by the Day 48 of observations. Microscopic investigation of the sample was in full agreement with the droplet size distribution analysis, clearly indicating increasing coalescence within the system, starting from the second day of ageing. The sample remained stable for a short period after 50 days of ageing, with first signs of phase separation observed at Day 57. Full system degradation in the form of emulsion phase separation took place by Day 63 of the investigation.

Figure 4.36 presents a summary of experimental data collected from droplet size distribution analysis and microscopic investigation of the system comprising laboratory grade Dodecane as the media of its continuous phase. The resultant emulsion contained 87.9% of dispersed phase by total weight. The sample demonstrated a fair stability over 50 days of ageing. Slow progressing gradual coalescence has been observed throughout the entire investigation period. Unlike the sample prepared using Parprol oil, the one under discussion did not contain a distinct separation between the two types of droplets within the system, the larger coalesced ones and the non-coalesced ones.

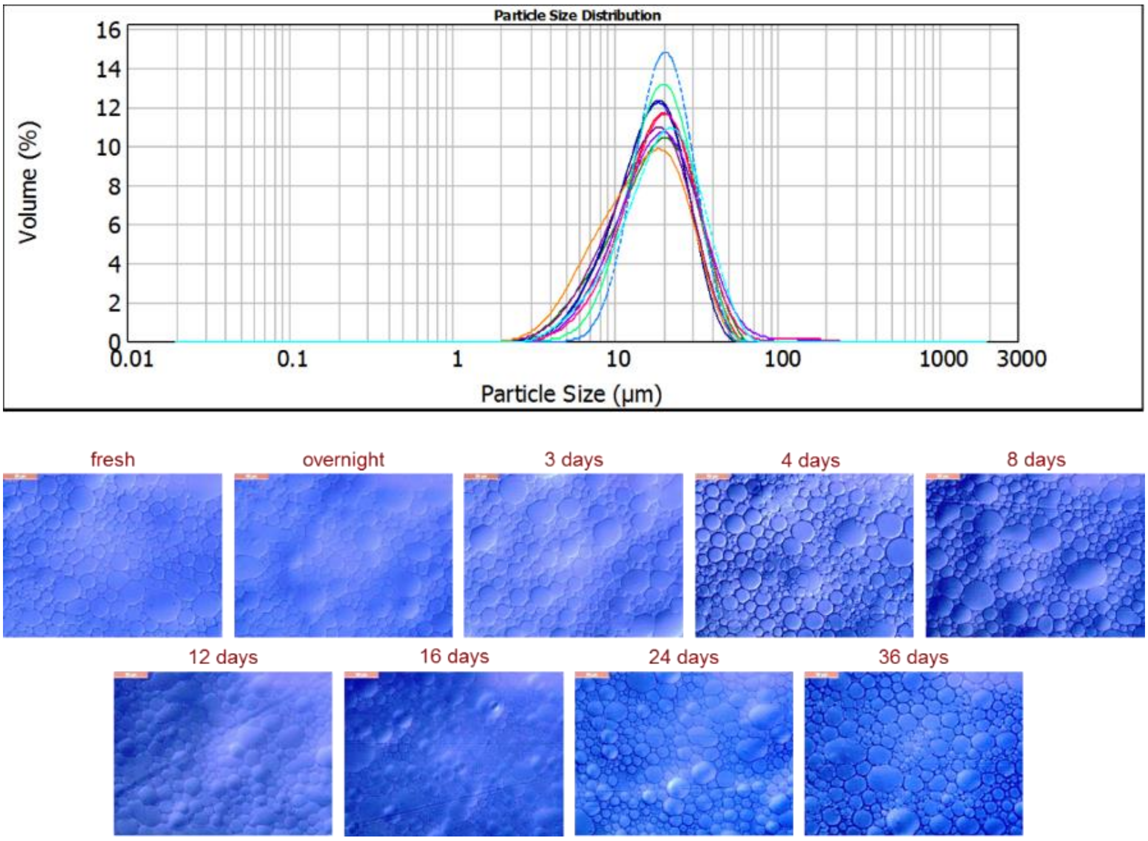


Figure 4.36: Droplet size distribution curves and respective microscopic images at various stages of ageing for the sample prepared using amine (AM0275) POSS nanomolecules with laboratory grade Dodecane

An even increase of droplet size was observed throughout the system, indicated by a slow broadening of the droplet size distribution curve with ageing. No peak shifts or formations of secondary peaks in the droplet size region closer to 100 microns were observed. Microscopic investigation of emulsion confirmed the findings of the droplet size distribution analysis. A gradual increase of droplet size throughout the sample is clearly observed on the microscopic photos at different stages of ageing. It is critical to note that the sample became too unstable under shear after Day 36 of ageing, rendering any further microscopic investigation impossible. The system underwent a complete degradation in the form of emulsion phase separation by Day 58 of the investigation.

The data collected as a result of experimental investigation conducted using aminoethylaminopropylisobutyl POSS nanomolecules and further discussion revealed very important findings. We ascertained that these molecules contain a very high capacity for the formation and stabilisation of highly concentrated emulsions when used alone as an exclusive stabilising agent. This was true across all oil types used within the frame of this current study. The stability results varied with various oil properties used as the dissolution media; however, as compared to all the other types of POSS nanomolecules studied previously, AM0275 POSS yielded exceptional stability of the system both on ageing and under shear. The highest stability was obtained in the system prepared using low viscosity and low aromatic content Mosspar-H oil as part of the continuous phase. The sample remained stable until Day 288 of ageing. It is important to note that this was the most recently available data at the point of discussion of results. The resultant sample did not undergo destabilisation and remained stable further past the mentioned time. However, since Day 288 was already an exceptional result indicating extremely high stability of the system, both on shelf and under shear, further investigation was not necessary for practical purposes.

Emulsion stabilised using a similar low viscosity, but high aromatic content Ash-H oil demonstrated a drastic decrease of stability as compared to Mosspar-H. The sample remained stable with no signs of coalescence or other destabilisation within the system up until Day 96 of ageing. However, analysis performed at 144 days indicated a partial crystallisation of the dispersed phase of emulsion. This was evident from microscopy as well as droplet size distribution curves. Both emulsions prepared with the use of high viscosity and high aromatic content Parprol oil, as well as laboratory grade Dodecane, demonstrated similar stability results of the system. Moderate stability was observed for both samples with full emulsion phase separation occurring shortly after Day 50 of ageing. For emulsion comprising Parprol oil as part of its continuous phase, a stepwise fairly aggressive coalescence occurring within the system was observed; on the other hand, the system prepared with laboratory grade Dodecane demonstrated a very slow even and gradual coalescence progression throughout the investigation. Unlike the Parprol oil sample, however, this system became highly unstable under shear after Day 36 of ageing.

Overall, AM0275 POSS molecules, as compared to all the other types of these compounds investigated previously demonstrated a very high ability to act as a stabilising agent for the highly concentrated emulsions. This was true both for stability to coalescence and ageing stability. It was determined experimentally that the most optimal media for these molecules providing best conditions towards the interaction with the system is the low viscosity hydrocarbon oil with low aromatic content. Such exceptional results obtained using these type of nanomolecules can be attributed to a number of factors, a major one being the presence of the reactive bridging secondary amine within the functional group in addition to the terminal primary amine. It was already obtained previously that amino POSS nanomolecules provide the best stability as compared to molecules containing other types of functional groups, and in the case of AM0275, the presence of a more reactive amine in addition to the less reactive results in a drastic increase of stabilising properties. Moreover, aminoethylaminopropylisobutyl contains a shorter length i-butyl hydrocarbon chain R-group which, as discovered previously, is more favourable for stabilisation of the system since it eliminates the possible steric hindrance between the individual molecules, both at the interface and in the inter droplet layer.

Due to all discussions in this section focusing on aminoethylaminopropylisobutyl POSS nanomolecules, this compound, in combination with low viscous and low aromatic content Mosspar-H oil, were separated as a stabilising system for further experimental work and investigation.

4.4 ABILITY OF AMINOETHYLAMINOPROPYLISOBUTYL POSS NANOMOLECULES TO FORM AND STABILISE BULK HIGHLY CONCENTRATED EMULSIONS

The previous section of the current investigation focused on the general ability of POSS nanomolecules towards the formation and stabilisation of the system of interest. A comprehensive study was performed to determine the compounds most suitable for this purpose. Figure 4.37 presents a brief overview of results obtained throughout the study until this point. This current section focuses on the results and discussion of the experimentally obtained information on the ability of AM0275 POSS nanomolecules in combination with Mosspar-H hydrocarbon oil towards the formation and stabilisation of highly concentrated bulk emulsions. The principal difference of this system from the one that was the focus of preceding experiments is the concentration of the ammonium nitrate solution used as a dispersed phase.

In the case of bulk emulsion, an 80% aqueous ammonium nitrate solution is used in the system as opposed to 60% solution used for preparation of small batch experimental samples. Such a high concentration of ammonium nitrate within the dispersed phase puts temperature limitations on the emulsion preparation process and results in dispersed phase existing in the super cooled state at ambient temperatures. Such a system is a highly concentrated emulsion (HCE) with super cooled dispersed phase. Total aqueous phase concentration used in bulk emulsion was set at 90%, as in previous experimental work.

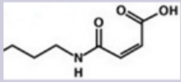
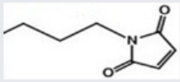
POSS Type	Mosspar-H	Ash-H	Parprol	Dodecane
AL0130	Separation - 30 minutes	Separation - 30 minutes	Not Forming	Not Forming
MA0701	Not Forming	Not Forming	Not Forming	Not Forming
CA0296 	Significant coalescence overnight Separation – 2 days	Significant coalescence overnight Separation – 10 days	🚫	🚫
IM0673 	Immediate significant coalescence Separation – 2 days	Significant coalescence – 8 days Separation – 10 days	Immediate significant coalescence Separation – overnight	Immediate significant coalescence Separation – overnight
AM265 	12 days Significant coalescence – 16 days	Significant coalescence – 3 days Separation – 8 days	>50 days (slow progressing coalescence)	Immediate significant coalescence Separation – overnight
AM270 	Immediate significant coalescence Separation – overnight	Significant coalescence – 3 days Separation – 4 days	Immediate significant coalescence Separation – 10 days	Immediate coalescence Separation – overnight
AM0275 	>200 days	>100 days	Stable for >50 (moderately progressing coalescence)	Stable for >50 (slow progressing coalescence)

Figure 4.37: Overview of stability results obtained throughout the investigation on POSS nanomolecules' ability towards formation and stabilisation of the system of interest

This, however, was a fixed amount added on preparation to the continuous phase, as opposed to slow addition of dispersed phase until structure change occurred within the system for small batch experiments. Emulsion preparation was performed in a heated environment at 80°C with the use of Hobart N50 mixer.

The main purpose of this aspect of the experimental work was to build upon and complement results obtained previously. The focus was on the investigation of the ability of AM0275 compound dissolved in the Mosspar-H oil to form and stabilise the commercial bulk highly concentrated emulsion with super cooled dispersed phase, both solely and as a co-surfactant in combination with industrially used PIBSA-Mea surfactant. Shelf life under shear, and shelf life of the system after shearing stability, were both investigated. Double cylinder pumping system with a 2mm diameter orifice was used for the purposes of shearing. Emulsion was pumped two times at a pressure of 1 bar. The resultant sample was investigated and followed microscopically.

4.4.1 Formation and stabilisation of HCE with super cooled dispersed phase with the use of Aminoethylaminopropylisobutyl POSS solely

Before introducing AM0275 POSS molecules into the system as a co-surfactant in combination with industrially used surfactant, it was vitally important to investigate the ability of this compound to form and stabilise the system without the presence of additional stabilisers. As in previous experimental work performed as part of the study, the total concentration of POSS molecules used was 6% by weight of oil phase. The continuous phase of emulsion comprised aminoethylaminopropylisobutyl dissolved in low viscous and low aromatic content Mosspar-H oil. This was placed into a preparation bowl heated to 85^{o}C of a Hobart N50 agitator. A supersaturated solution of dispersed phase required a prior heating to 80^{o}C in order for successive dissolution of ammonium nitrate at a concentration of 80%. This solution was then added gradually at a slow agitation rate to the oil phase which was performed straight on dissolution, while the temperature remained above the point of ammonium nitrate crystallisation of 65^{o}C. As soon as the addition of an aqueous phase was completed, the rate of mixing was increased to accommodate system formation and further refinement to a required droplet size of approximately 10 micron. A sample was taken at various stages of refinement to follow the droplet size distribution within emulsion and ensure the required droplet size is obtained. This, however, was not the case for the performed experiment, as explained in further discussion.

Emulsion formation with the use of AM0275 nanomolecules solely was possible, with a sample of the resultant system illustrated in Figure 4.38(a). However, as soon as the first sample was taken for the purposes of droplet size distribution analysis, it was discovered that crystallisation of the dispersed phase within the system occurred immediately on cooling of the sample to a temperature below 65^{o}C, as demonstrated in Figure 4.38(b), rendering any further analysis and capturing of the system refinement time impossible.

Continuous refinement of emulsion was performed further, to establish the general stability of the system on shearing. Structural degradation of the sample in the form of partial oil phase separation occurred after 10 minutes of refinement at high agitation rate, as demonstrated in Figure 4.39.

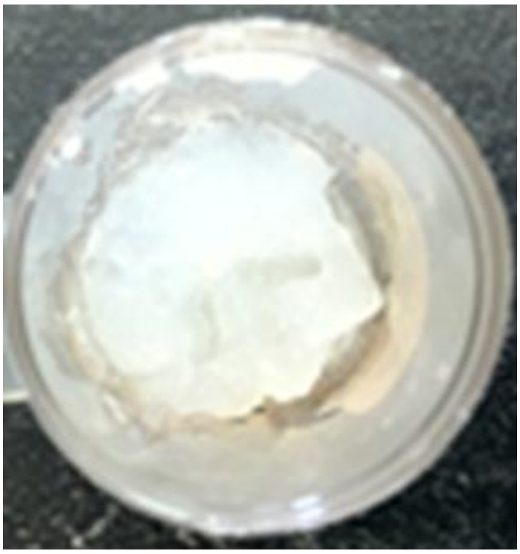


Figure 4.38 (a): HCE with super cooled dispersed phase formed with the use of AM0275 POSS molecules solely

The experiment demonstrated that aminoethylaminopropylisobutyl POSS nanomolecules *do* have a capacity towards the formation of highly concentrated emulsions with super cooled dispersed phase. This is attributed to the gelling phenomenon occurring at the border of two phases. This is a stabilisation by the means of physical nature with formation of the stable rigid barrier at the interface. However, it was revealed that the system underwent dispersed phase crystallisation as soon as the temperature dropped below 65^{o}C, demonstrating that nanomolecules under consideration *do not* contain the required capacity towards the stabilisation of the dispersed phase against crystallisation of the ammonium nitrate on cooling.

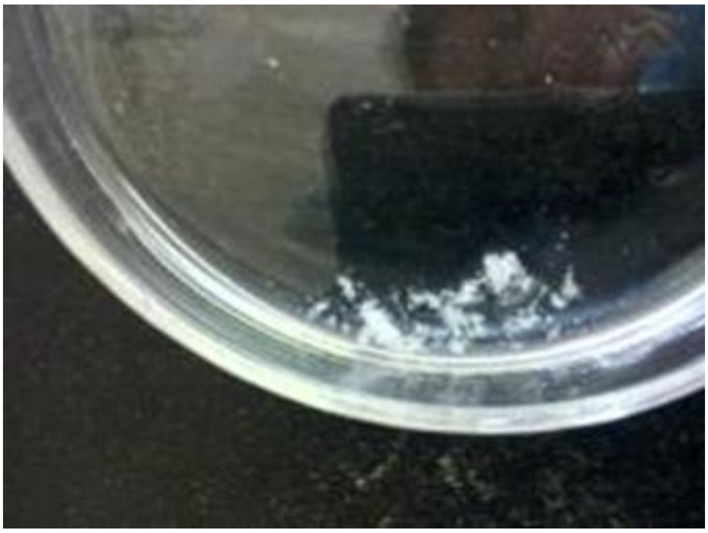


Figure 4.38 (b): Crystallisation on cooling of the HCE with super cooled dispersed phase formed with the use of AM0275 POSS molecules solely

Figure 4.39: Degradation of the HCE with super cooled dispersed phase formed with the use of AM0275 POSS molecules solely

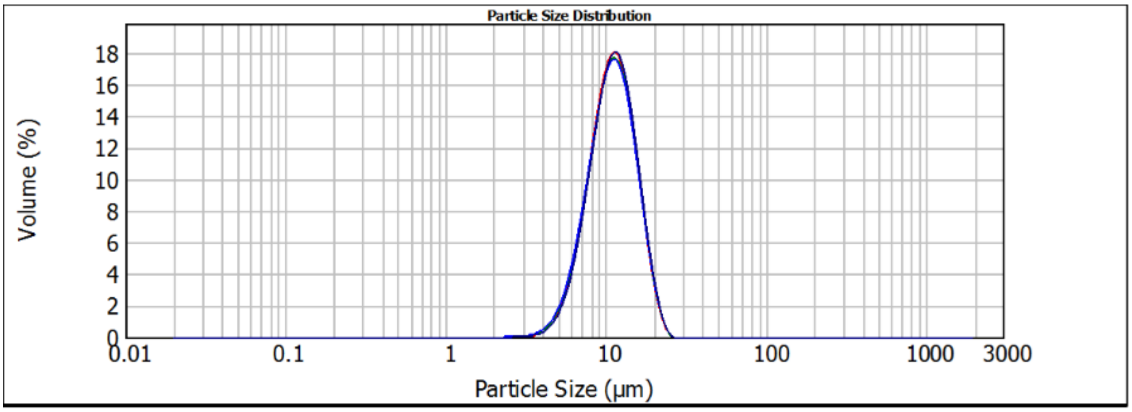
Since unlike the 60% concentrated aqueous solution used for preparation of small batch samples, 80% concentrated is a supersaturated solution, ammonium nitrate may be dissolved only under two condition: 1) maintain the temperature of solution elevated above the temperature of crystallisation of ammonium nitrate, 65°C, and 2) maintain the solution in a super cooled state at the ambient temperature which is the mechanism utilised in bulk HCE. This is achieved via the use of stabilisers by means of constant dynamic hydrogen bond formation and breaking with the ammonium nitrate molecules within the aqueous phase. This illustrates that the said nanomolecules have a very low degree of interaction and hydrogen bonding with ammonium nitrate molecules. Such behaviour, in turn, may be explained by the formation of the rigid gel-like barrier across the interface of two phases which prevents any such interactions from happening, resulting in the AM0275 POSS ability towards emulsion formation with a complete inability to provide system stability under ambient conditions. Additionally, continuous refinement analysis of the system has demonstrated a fair degree of the said emulsion to withstand shearing stress, emphasising once again both the rigidity and flexibility of the formed interfacial layer.

As a result of the data collected during this experimental work, certain very important points have been revealed and discussed about the aminoethylaminopropylisobutyl POSS nanomolecules as a potential surfactant for bulk industrially manufactured HCE with super cooled dispersed phase. These molecules have an ability to partially stabilise emulsion. Therefore, an aid of a more conventional and widely implemented surfactant, used in combination with AM0275, became necessary for formation of a system that met all stability requirements.

4.4.2 Formation and stabilisation of HCE with super cooled dispersed phase with the use of AM0275 POSS in combination with PIBSA-Mea

The aim of this section of the study was to investigate the ability of the combined system comprising aminoethylaminopropylisobutyl POSS nanomolecules and PIBSA-Mea surfactant to form and successfully stabilise bulk HCE with super cooled dispersed phase. Furthermore, the goal was to achieve the said by lowering the standard total concentration of PIBSA-Mea stabiliser when used solely during industrial manufacturing of bulk emulsion. The amount of the standard stabiliser used within the frame of experimental work presented was 10% by weight in oil phase as opposed to 17% used in manufacturing. POSS molecules carried the role of a co-surfactant within the stabilising system, added in concentrations of 0.1% by weight of continuous phase. The remaining components, preparation procedures and conditions were identical to those discussed previously. A reference sample comprising 10% of PIBSA-Mea surfactant within the oil phase was prepared for comparison purposes to investigate the effects of addition of nanomolecules on various aspects of emulsion manufacturing and stability.

Successive formation of both the reference emulsion and the one containing AM0275 POSS molecules as a co-surfactant was possible. Additionally, both samples were successfully refined to the dispersed phase droplet size of 10 micron. A comparison of refinement times and droplet size distribution curves is demonstrated in Figure 4.40.



Sample	$t_{refinement}$
Pibsa	45
Pibsa + AM0275	40

Figure 4.40: Emulsion refinement time comparison along with droplet size distribution curves of reference sample and sample containing AM0275 POSS as co-surfactant

It was obtained that the addition of POSS nanomolecules as a co-surfactant had no significant effect on either the emulsion refinement time or droplet size distribution profile. Refinement time of the reference sample yielded 45 minutes, whereas the one of the sample containing AM0275 compound as a co-surfactant resulted in 40 minutes. At such a fairly high refinement time values, it is impossible to attribute with confidence the difference in the said value between the two samples to the presence of nanomolecules in the system. This difference fits within the normal general uncertainty due to external fluctuating factors of the environment and hence may be considered as a result of these fluctuations. Inspection of droplet size distribution curves for both samples clearly illustrates that both curves are similar with the slight difference being only insignificant. This is attributed to the uncertainty between the individual test runs on the analytical equipment rather than the effect of the addition of POSS compound into the stabilising system.

Results of the microscopic investigation of fresh unpumped samples for both the reference emulsion and the one containing AM0275 compound as part of the stabilising system are presented in comparison in Figure 4.41. It was clearly observed that the sample containing 10% of PIBSA-Mea surfactant only as a stabiliser showed moderate crystallisation of the dispersed phase straight after preparation. This result was expected since it was known that the minimal amount of the used emulsifier required to successfully stabilise the system under the study is 17% by weight in oil phase. There were simply not enough surfactant molecules within the system to accommodate full stabilisation against the crystallisation of dispersed phase. An addition of as little as 0.1% by weight of oil phase of the said POSS nanomolecules resulted in full stabilisation of the system. It can be seen clearly that the sample containing these molecules as a co-surfactant remained uncompromised structurally by ammonium nitrate crystallisation occurring within individual drops of dispersed phase solution.

Both samples have been followed by means of further microscopic observations for a total of 45 days. At the point of reporting, this was the most recent available ageing data and hence this point of investigation was considered to be the end point. This was also caused by investigation of shelf life of the system on a long term basis falling outside the scope of work. Within the framework of the current study, any further follow up of the samples would become impractical. Slow progression of crystallisation occurred in the reference sample between the day of preparation and the final follow up day. As assumed, samples containing AM0275 nanomolecules remained fully stable throughout the entire time period.

A similar trend was observed when resultant emulsions were subjected to shear by the means of pumping. This has been done to mimic the conditions a system undergoes on an industrial level during transportation to the storage site prior to subsequent storage.

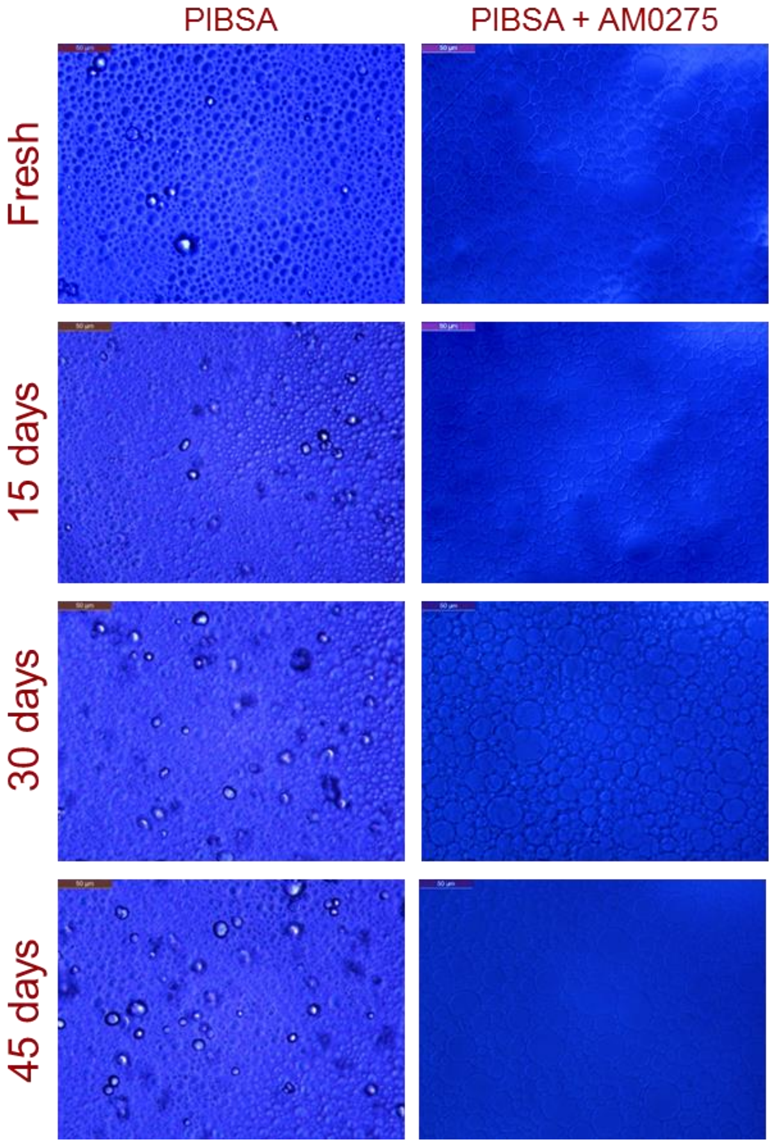


Figure 4.41: Comparison microscopic investigation of unpumped reference sample containing PIBSA-Mea only as well as the sample containing POSS molecules within oil phase

The investigation of both pumping and storage stability of the pumped system was of high importance. Microscopic results of said investigation are presented in Figure 4.42. Since, as was discussed previously, an unpumped system containing 10% of PIBSA-Mea as the only means of stabilisation demonstrated crystallisation of the dispersed phase immediately on preparation, pumping of this emulsion only further increased destabilisation. It is important to note, however, that no dramatic increase of crystallisation of dispersed phase was observed upon subjecting the system to shearing. As before, the ageing stability of both samples has been followed via the means of microscopic analysis for a total of 45 days.

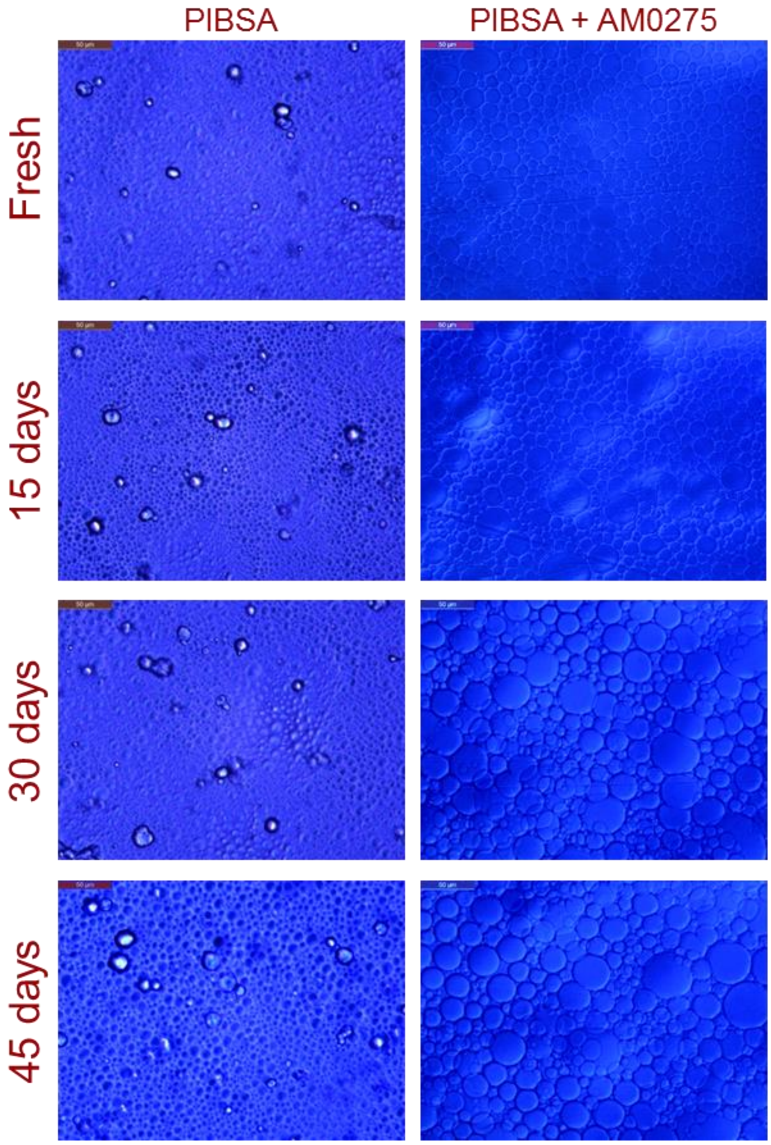


Figure 4.42: Comparison microscopic investigation of pumped reference sample containing PIBSA-Mea only as well as the sample containing POSS molecules within oil phase

Throughout the observation period, an increase of crystallisation within the sample containing only surfactant as stabiliser was observed.

Emulsion stabilised with the system containing AM0275 POSS nanomolecules as a co-surfactant in addition to PIBSA-Mea underwent pumping successfully. No destabilisation within the structure was observed; this applied to both crystallisation of dispersed phase as well as coalescence of the individual droplets. Moreover, throughout the investigation of the shelf life stability of this emulsion, it demonstrated no crystallisation taking place until 45 days. Slight droplet coalescence was observed from Day 30 of the observations; however, analysis of the sample at Day 45 proved this to be a very slow proceeding process. The degree of coalescence that took place was moderate and would not have any drastic impact on the properties of the product on industrial scale production.

From all discussed, it was clear that the addition of aminoethylaminopropylisobutyl POSS nanomolecules to the conventional PIBSA-Mea surfactant has a drastic effect on the under shear stability of the system under investigation and further shelf life stability after the system has been subject to the said shear in the form of pumping under pressure.

AM0275 compound, when used in the multi surfactant system in combination with PIBSA-Mea stabiliser, has demonstrated a high ability towards improving both shelf life and under shear stability of highly concentrated emulsion with super cooled dispersed phase. This is attributed to the ability of these nanomolecules to form a rigid gel film across the interface of the two immiscible liquids, effectively encapsulating the individual droplets of dispersed phase and preventing destabilisation of the interface. As was demonstrated when used solely, such molecules could not provide the overall stabilisation of the system since only stabilisation of the interface was occurring. When used in combination with surfactant, however, nanomolecules provide successive and effective stabilisation of the interface, whereas PIBSA-Mea molecules stabilise the inter-droplet layer via the formation of the micelles, a phenomena explained earlier. Another highly important finding and advantage of the addition of the AM0275 molecules as a co-surfactant is that the presence of these compounds allows drastic decrease of the amount of PIBSA-Mea required for successive stabilisation of emulsion, as compared to the currently adopted standard amount, rendering final product significantly more cost effective.

CHAPTER 5

Summary and Conclusion

This present study investigated the possibility of implementation of POSS nanomolecules as a stabiliser, or one of the components of the stabilising system, in the highly concentrated emulsions and highly concentrated emulsions with super cooled dispersed phase. This has not been attempted previously; therefore, the main goal was to investigate the possibility of such implementation as well as lay the ground work for further developments. Fundamental questions raised and answered as part of the investigation were as follows:

- Do POSS nanomolecules possess the capacity towards the formation of the highly concentrated emulsions?

- If emulsion formation with these chemical compounds is possible, what is the ability towards the stabilisation of the system both on the shelf and under shear?

- Which types of molecules considered are most compatible with the system under investigation?

- If these compounds are not able to provide the desired stability of the system when used solely, what are the effects on stability when used as a co-surfactant with a conventional emulsifier?

Several types of industrial grade oils, possessing various viscosity and aromatic content properties, were used as continuous phase media: Ash-H, Mosspar-H and Parprol. In addition, one pure laboratory grade oil, Dodecane, was taken for comparison purposes. This was done to investigate the possible effects of the media properties on the activity of molecules and distinguish the oil most suitable and most advantageous for achieving the best stability of the system.

As a starting point of experimental work and study, it was necessary to investigate the surface activity of the said compounds within the system of interest. This was done to determine whether or not the nanomolecules considered demonstrate any activity with other components of the system, hence are not inert within the system which would render any further investigation impossible. Interfacial tension measurements at the boundary of two phases comprising the system were performed in the presence of POSS molecules within the oil phase as the only stabilising component; results were compared against the interfacial tension between phases without the presence of any stabiliser. Obtained results demonstrated that nanomolecules were indeed surface active in the system and the presence of these compounds resulted in the drop of interfacial tension as compared to the reference values. This was true for all of the POSS nanomolecules investigated. During the interfacial tension measurements, it was observed that one of the investigated POSS nanomolecules, the aminoethylaminopropylisobutyl (AM0275) POSS, induced the formation of a fairly rigid gel-like barrier across the aqueous oil interface. This occurred only at the region of two phases coming into contact and did not affect the internal structure of either of them. Moreover, it was demonstrated that the presence of POSS nanomolecules did not affect the overall viscosity of the continuous phase of emulsion.

After the surface activity of said compounds was confirmed, the focus of experimental work shifted onto the ability of nanomolecules towards the formation and further stabilisation of highly concentrated emulsions solely. For this stage of work a small batch highly concentrated emulsions were prepared. The goal was to investigate which types of nanomolecules, of the ones considered, were most suitable for the above mentioned purposes. It was determined that POSS nanomolecules containing terminal primary and bridging secondary amine functional groups in combination with the short hydrocarbon chain length i-butyl R-group provided the best stability of the system. Emulsions formed and stabilised with the use of these molecules demonstrated the stability of the system both on shelf and under shear of 288 days, at which point any further follow up did not have practical purpose. These were the same POSS molecules, the aminoethylaminopropylisobutyl (AM0275) POSS, that induced the gelation of the interface between the two phases of emulsion, effectively providing additional means of stabilisation. The rest of the POSS compounds resulted in a much lower stability, ranging from overnight degradation to approximately 100 days. For the said sample, such a high stability of the system was reached in combination with low viscosity and low aromatic content Mosspar-H oil. This stabilising system, as the most promising, was chosen for further work.

The final stage of the study entailed the investigation of the ability of POSS nanomolecules towards the stabilisation of highly concentrated emulsions with super cooled dispersed phase, the system used on the industrial level production as opposed to the small batch highly concentrated emulsions found at laboratory scale. The stabilising system for this emulsion, as was mentioned previously, comprised the AM0275 POSS nanomolecules within the Mosspar-H oil. It was determined that emulsion formation was possible with these molecules; however, such an emulsion proved to be highly unstable with separation taking place immediately after preparation. After this discovery, it became necessary to formulate the stabilising system containing AM0275 molecules as a co-surfactant in combination with a standard PIBSA-Mea stabiliser used for stabilisation of emulsions on industrial level production. The addition of as little as 0.1% by weight in oil phase of the said compound to standard formulation allowed for the decrease of surfactant in the standard formulation from 17% by weight in oil phase to 10%, without compromising both shelf life and under shear stability. This effectively provides a new formulation for stabilisation that makes highly concentrated emulsions with super cooled dispersed phase both more environmentally friendly and more cost effective.

This study has investigated the new and unexplored field of using POSS nanomolecules for stabilisation of emulsions, effectively laying crucial ground work allowing for successive investigation, understanding and implementation of these molecules in a whole variety of fields with a spectre of potential advantages over the currently adopted stabilising formulations. It was determined that POSS nanomolecules have the capacity to both form and stabilise an emulsion. Furthermore, it was demonstrated that both the functional group of the said compounds, as well as the R-group, have a crucial effect on the above mentioned properties. This finding demonstrates that, due to the availability of a whole range of various molecules with different types of functional groups as well as the ability to design molecules to suit particular systems, implementation of such compounds is not limited to a specific industry but is rather possible in any system of emulsion type regardless of the field of use.

Implementation of such compounds carries large potential environmental and cost benefits. While the main thrust of this study rests with the explosives industries where both long term storage and pipeline pumping are economically viable options along with environmental considerations, the actual and practical findings of this study could benefit a wide range of industries, such as but not limited to mining, explosives, pharmaceutical, cosmetics and food industries, which use emulsions as either a mode of transportation or a process ingredient due to the need for product storage or a final product.

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