

Wax Anti-Settling Additives

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Declaration

This dissertation is the result of my own work and includes nothing which is the outcome of work done in collaboration except where specified in the text.

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It does not exceed the prescribed word limit of 65 000 words, including tables and footnotes.

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Abstract

Wax anti-settling additives (WASA) are used to mitigate against the problems caused by the settling of *n*-alkane wax crystals, which crystallise from petroleum diesel. This can result in the blocking of fuel filters and hence vehicle failure. However, the mode of action for such additives is not currently known and two mechanisms have been proposed: they reduce the wax crystal size to such an extent that they settle very slowly; or they induce gelation in the wax suspension. This project aims to elucidate the mechanism of WASA within the diesel system.

A room temperature crystallising model diesel (10 wt% *n*-alkanes in dodecane) has been developed. This model system has given a good response to the additives, with the wax crystals reduced in size, and is hence suitable for mechanistic studies. Differential scanning calorimetry and infra-red spectroscopy both suggest that the WASA is incorporated in or onto the wax crystal. DSC shows that small amounts of WASA suppress the wax crystallisation temperature and change the shape of the heat flow curve. FT-IR shows the WASA amide stretch present within filtered and dried wax crystals.

Intriguingly, electrophoresis experiments show that the WASA imparts a positive charge to the wax crystals, suggesting an electrostatic role in the WASA action. Rheological experiments show the presence of a weak gel in the WASA doped model diesel. However, the gel strength is not altered by the presence of an organic salt and thus cannot be purely electrostatic in origin.

Small angle neutron scattering has been conducted to help locate the WASA in the system. It has shown that in solution WASA shows a collapsed polymer coil structure with a single molecule occupying a 28 Å diameter sphere and multiple WASA molecules forming a 2400 Å diameter sphere. In the presence of the wax the WASA scatter does not significantly change suggesting that the WASA is on the surface of the wax crystal.

By combining these results, a mechanism of WASA action is proposed as WASA cations interactions bridging between the wax crystals causing a weak bridging flocculation gel with electrostatic and steric effects contributing to stabilisation. The WASA charges are partially dissociated thus giving the electrophoretic effect and the long chains on the cations can contribute to stability *via* steric stabilisation.

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1 Introduction

1.1 Infineum

Infineum International Ltd. is a world leader in the formulation and manufacturing of petroleum additives for lubricants and fuels. Formed in 1999 as a joint venture between ExxonMobil and Shell, Infineum has grown into a global company. They are currently the market leader in cold-flow operability additives.¹ These fuel additives help to overcome issues arising from the use of diesel in cold climates and conditions.

1.2 Diesel Engine

Diesel engines operate *via* a fuel injector system whereby fuel is injected into the engine under very high pressure (roughly 9.2 MPa) and ignites. This system is used to achieve more complete combustion and reduced particulate, nitrogen oxide and sulphur emissions.² The mechanical clearances of this injection equipment are typically 2.5 μm ,³ so the presence of any contaminants under high pressure can be disastrous. The most damaging contaminants are abrasive particles in the 5 – 20 μm range.⁴ Water can also have a seriously damaging effect due to its facilitation of corrosion, microbial growth and ability to plug injection systems *via* freezing. Water enters the fuel due to precipitation, humidity and condensation and can be present in the fuel as free, emulsified or dissolved water.⁵ A limit of 200 ppm for emulsified or dissolved water and a “no free water” tolerance for diesel fuel were set by the European Union in 2005.²

To protect this delicate system, a series of filters are used: main filters to remove general debris; ‘sedimentors’ to remove water and contaminants *via* sedimentation; and ‘agglomerators’ to separate emulsified water from fuel.⁴ Filter holes can be as large as 100 μm but 150 – 200 μm in depth with many fibre layers, so can catch most 10 – 15 μm sized particle contaminants.³ The use of these filters creates problems due to wax crystallising from diesel at lower operational temperatures.

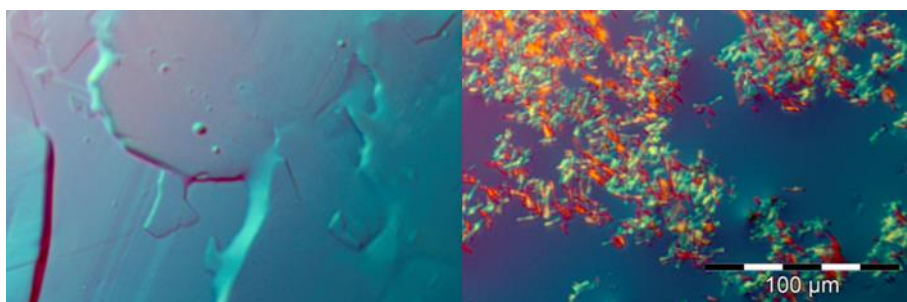
1.3 Cold-flow properties and problems for diesel

Middle distillate fuel, from which diesel is derived, is a complex hydrocarbon mixture typically made up of alkenes, cycloalkanes, aromatics and 15 – 30 % long

chain *n*-alkanes. The composition depends on the refining process and the crude oil source.⁶ The length distribution of the *n*-alkanes is complex with chain lengths ranging between 9 – 40 carbons.⁶ The high molecular weight *n*-alkanes are vital for efficient pressure-induced fuel auto-ignition; however, they cause problems at low temperatures by crystallising from the fuel. These wax crystals grow as orthorhombic plates up to 1 mm in size and can thus block fine engine filters,³ causing engine fuel starvation and failure. In addition, physical interactions between the individual crystals can result in the formation of a gel; as little as 0.5 – 1 wt% concentration of precipitated wax can cause the fuel to solidify.³ The treatment of diesel fuel to improve its cold-flow properties remains a problem for the petroleum and transport industries.

To combat this problem, middle distillate flow improvers (MDFIs) were developed to alter wax crystal morphology from large plates to more favourable forms, such as smaller needles (Figure 1.1). The irregular packing of these smaller needle-like crystals form porous filter cakes on engine filters, which allows fuel to flow to the pump and injectors, thus preventing engine failure.⁷

The effectiveness of MDFIs is assessed by three characteristic temperatures: the cloud point (CP), pour point (PP) and cold filter plugging point (CFPP). The CP is the temperature at which the first wax crystals become visible to the human eye by inspection upon cooling. The PP is the temperature at which the wax structure is sufficient to cause the fuel to gel, measured by optical tilt methods. The CFPP is the temperature at which 20 ml of fuel will not flow through a fine wire mesh filter in under 60 seconds while under vacuum.⁶



*Figure 1.1: Photomicrographs showing large *n*-alkane plates from untreated diesel (left) and small needles from diesel treated with 400 ppm of middle distillate flow improvers (right), both have the same scale.*

However, the crystal modification causes the further problem of wax settling. Wax crystals have a higher density than the fuel from which they precipitate. MDFI modified crystals are less likely to gel, so the slurry in fuel remains lower in overall

viscosity and the settling rate is increased. If the fuel is stored below its cloud point (CP) for a long period, the wax settles to the bottom portion of the storage container causing wax enrichment in the lower portion of the fuel (Figure 1.2). Wax enriched layers will have a higher CP while the top wax reduced layers will have a lower CP. Thus, when the fuel is discharged from the storage container it will have differing CPs over the discharge time, lowering the fuels' quality and cold-flow reliability. As such, wax anti-settling additives (WASAs) are needed to keep wax crystals dispersed in the fuel.⁸

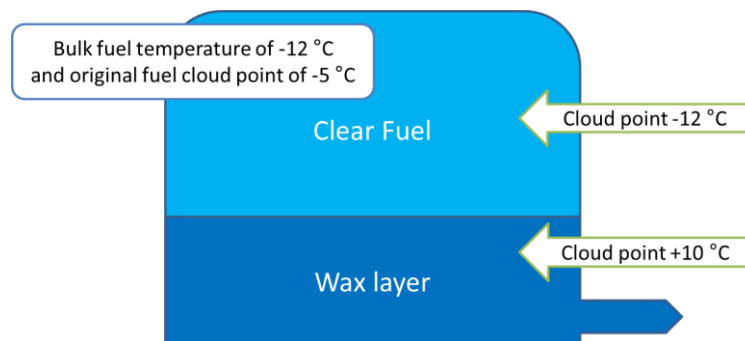


Figure 1.2: Schematic depicting the wax settling in a diesel storage container kept below the fuel's cloud point.

The global demand for renewable energy sources is growing and the replacement of petroleum diesel with biodiesel is expected to increase by 10% by 2020.⁹ Unfortunately biodiesel displays poor cold-flow properties with CPs and PPs about 15 to 25 °C higher than that of petroleum diesel. In addition, MDFIs are less effective in biodiesel than diesel. Biodiesel consists of fatty acid methyl esters, ethyl esters and a mixture of different hydrocarbon components. The increase in CP and PP is thought to be due to methyl esters, particularly methyl palmitate ($C_{17}H_{34}O_2$) and methyl stearate ($C_{19}H_{38}O_2$).¹⁰ It has been suggested that these co-crystallise with *n*-alkanes of matching chain length (*n*-octadecane ($C_{18}H_{38}$) and *n*-eicosane ($C_{20}H_{42}$) respectively) worsening their cold-flow properties by making the wax crystal less receptive to the MDFIs.¹¹ The nucleation of these species can also strongly depend on the solvation environment and thus the petroleum diesel crude oil source which is blended with the biodiesel.¹²

1.4 Wax crystallisation

Wax crystallisation has two stages: nucleation and growth. Before a crystal can form, the solute (*n*-alkanes) must be in a state of supersaturation. A supersaturated solution has more dissolved solid than its equilibrium saturation and is therefore in thermodynamic equilibrium with the crystal solid. Work by Miers

and Isaac led to a metastable zone on the solubility-super solubility diagram shown in Figure 1.3.¹³

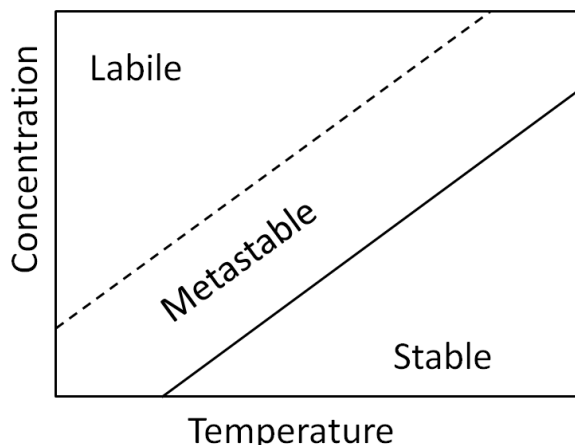


Figure 1.3: Generalised solubility-super solubility diagram with stable, metastable and labile zones. The solid line depicts the solubility curve and the dashed line depicts the super solubility curve.¹⁴

The diagram shows the stable zone, where crystallisation is impossible; the metastable zone, where spontaneous crystallisation is improbable but seeded crystallisation by nucleators is possible; and the labile zone, where spontaneous crystallisation is probable but not inevitable. The width of the metastable zone determines the supersaturation required, at a certain temperature, before a spontaneous nucleation event can take place. The super solubility curve is hard to define experimentally, as it is the point at which uncontrolled spontaneous crystallisation occurs. Its position is affected by the rate at which supersaturation is generated, intensity of agitation of the system, presence of trace impurities, and thermal history of the solution.¹⁴

If the condition of supersaturation is met, then the driving force for crystallisation is the difference in chemical potential, $\Delta\mu$, of the substance in its different states e.g. solution and crystal. However, supersaturation alone is not enough to cause crystallisation. Nucleation (providing a centre of crystallisation) must also either occur spontaneously or be induced. Nucleation can occur by agitation, extreme pressures, cavitation or by seeding with nucleators. Constituent molecules must coagulate and resist re-dissolving to form a crystal lattice. Because of the large number of molecules involved nucleation is unlikely to result from the simultaneous collision of all molecules required for the crystal formation. It may arise from bimolecular additions reaching a critical cluster size resulting in nucleation and crystal growth. This construction process needs to take place in an area of high supersaturation. Many clusters re-dissolve, but those above a critical nucleus

radius, r_c , are stable and form a crystal.¹⁴ The difficulty in studying nucleation arises from the fact that critical nuclei are typically only 100 – 1000 molecules large, so even if they are detected their structure might not be distinguished.¹⁵

Classical nucleation theory was originally based on the condensation of a vapour to a liquid, but can be extended as a simple model for crystallisation from melts and solutions:

$$\Delta G = \Delta G_S + \Delta G_V = 4\pi r^2 \gamma + \frac{4}{3}\pi r^3 \Delta G_v \quad 1.1$$

where ΔG – Gibbs free energy barrier to nuclei formation. ΔG_S – surface free energy, which is a positive quantity proportional to r^2 (r – radius of nuclei) assuming a spherical critical nucleus of r_c . ΔG_V – volume free energy, which is a negative quantity proportional to r^3 . ΔG_v – free energy change of the transformation per unit volume and γ – interfacial tension. For spontaneous crystal growth to occur, ΔG must be negative; this depends on the competition between ΔG_S and ΔG_V (Figure 1.4).

Many nuclei will re-dissolve, but those above a critical radius, r_c , remain stable and form a crystal. ΔG_S dominates when $r < r_c$ and favours re-dissolving, but at $r > r_c$ ΔG_V dominates and favours crystal growth.¹⁴ Davey *et al.* recently published a more detailed review on the nucleation of organic crystals. Differences between classical nucleation theory and experimental work have shown the inadequacies of this simple model with many of its assumptions found to be invalid. This has led to the development of new nucleation models such as two-step nucleation theory.¹⁶

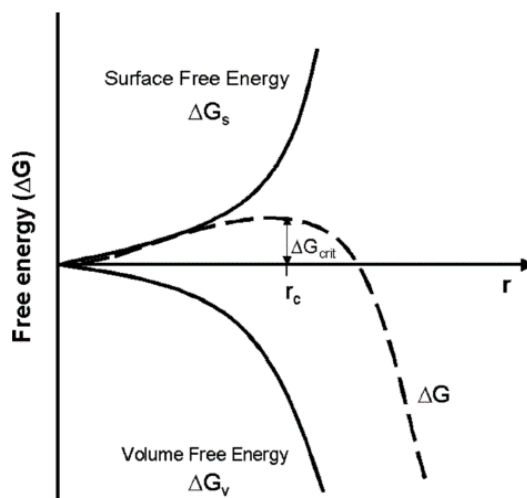


Figure 1.4: Free energy diagram for nucleation. Shows the competition between ΔG_V and ΔG_S . At r_c , the critical free energy ΔG_{crit} is reached so crystals can form.¹⁴

Volume and solvent effects, as well as the surrounding diffusion field all affect the rate of crystal growth. The dominant growth mechanism in operation depends upon many (and often interrelated) factors, e.g. the surface roughness or surface entropy of the crystal. If the surface is atomically smooth, there are so few sites for molecules to adsorb that growth is impossible until the (local) supersaturation increases. If the surface is very rough (e.g. lots of steps, kinks sites and dislocations) the diffusion of solute molecules from the surrounding solution controls the growth rate.

Wax crystal growth occurs by Burton, Cabrera and Frank's (BCF) theory (similar to spiral growth).¹⁷ The theory shows that a molecule diffuses towards a step fault and adsorbs; if incorporated at the site it forms the new fault site and attracts other molecules, thus continuing the crystal growth. The fastest growth proceeds *via* lateral stacking of the *n*-alkanes chains along their long axis (like toothpicks), perpendicular to the fastest growing crystal plane (Figure 1.5).¹⁸ From this process, an orthorhombic *n*-alkane wax crystal results, typically in the form of a thin truncated rhombus.

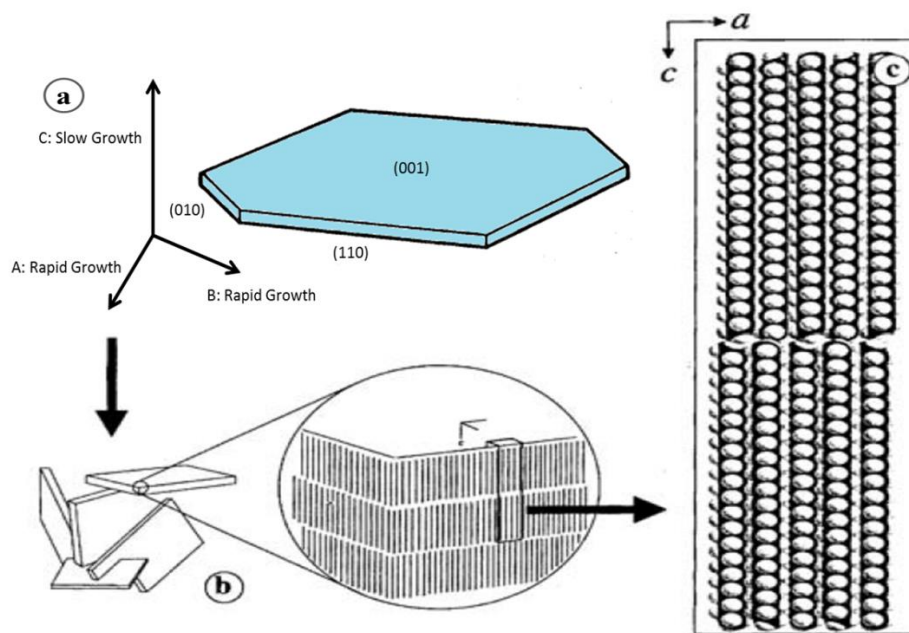


Figure 1.5: a) Schematic of a wax crystal plate depicting the planes and speeds of crystal growth, b) schematic of wax plates showing the *n*-alkanes molecular packing and c) the molecular packing of C_{36} within the one-dimensional multilayer wax crystal.¹⁹

As previously discussed, the crystal structure is an important contributing factor to the blocking of engine filters. Over 95% of *n*-alkane crystals from diesel fuel are of the flat, plate-like orthorhombic structure.³ One of the modern leaders of the field, Kevin Roberts *et.al.*,¹⁸ used high-resolution synchrotron X-ray powder diffraction

to characterise the *n*-alkanes crystals in the homologous series $C_{18}H_{28}$ to $C_{60}H_{122}$. They found that alkanes, C_nH_{2n+2} , generally adopt three structurally distinct groups: triclinic [$12 < n(\text{even}) < 26$], orthorhombic [$n(\text{even}) > 36$ and $n(\text{odd})$] and monoclinic [$28 < n(\text{even}) < 36$].²⁰ The crystals formed are thin plates with regular faces, in which the chain direction is more or less perpendicular to the lamella surface.¹⁸

They also showed that mixing large ranges of alkane chain lengths increased the amount of disorder in the inter-lamellae region between chain layers (Figure 6.1). Differences of just a few carbon atoms can cause protrusions into the inter-lamellae region. These chain ends can twist and bend, as they are no longer held by van der Waals constraints. This suggests that the large range of alkane chain lengths in diesel fuel leads to a large amount of disorder in the inter-lamellae region, which disrupts packing and hinders further nucleation along that plane. The system compensates by inter-chain mixing, which pushes the lamellae apart and thus produces kinks along the carbon backbone.¹⁸

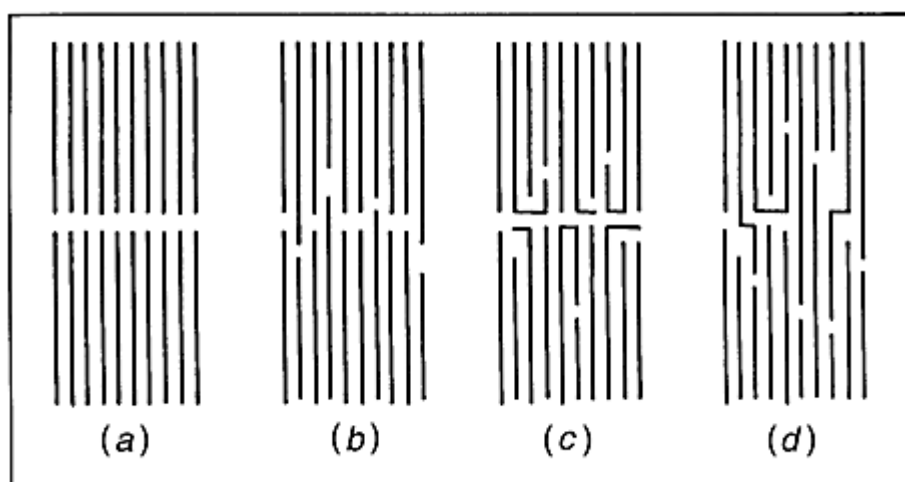


Figure 1.6: Schematic of inter-lamellae packing for: a) single alkane with a well ordered lamella region; b) small variance mixture of alkane chain lengths showing inter-chain mixing; c) high variance mixture of alkane chain lengths showing end-chain twisting and folding disorders; and d) high variance mixture of alkane chain lengths showing inter-chain mixing and end-chain bending/twisting at the lamella interface.¹⁸

Changing this plate morphology is of critical importance to preventing filter blockages and is done using a variety of MDFIs.²¹

MDFIs can be split into two main categories: nucleators and wax crystal growth inhibitors. Nucleators act by heterogeneous '3D' nucleation, lowering the energy barrier for nucleus formation by providing a suitable surface on which growth can occur, thus lowering the energy barrier to nucleation. It is essential that the

presence of nucleator species increases the number of nucleation sites, and thus many small crystals are formed (relative to a sample containing no nucleator). Wax crystal growth inhibitors change the crystal morphology by blocking some of the faster growing crystallographic faces by adsorption and/or co-crystallisation.²² These are typically polymeric materials. The two most common are ethylene-vinyl acetate copolymers (EVA) and comb polymers such as fumarate vinyl acetate copolymers (FVA). Along with WASAs, these will now be discussed in more depth.

1.5 Additives

1.5.1 Ethylene-vinyl acetate copolymers (EVA)

EVA, shown in Figure 1.7, was the first additive to be used to improve the cold-flow properties of diesel.²³ Two mechanisms have been proposed for EVA's interactions with *n*-alkane crystals: heterogeneous nucleation, and growth inhibition. Studies of the mechanisms of EVAs using differential scanning calorimetry (DSC),²² electron spin resonance²⁴ and computational molecular dynamics simulations²⁵ have shown cases of EVAs operating as nucleators or growth inhibitors, depending on the system involved. Studies have shown that EVA can decrease the pour point of diesel by 12 °C.²⁶ Various EVAs are utilised commercially by Infineum.

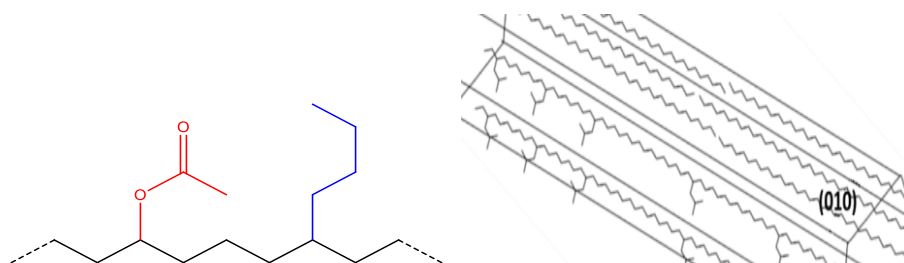


Figure 1.7: Left – general structure of an ethylene-vinyl acetate copolymer (EVA), vinyl acetate shown in red and random side branching shown in blue, Right – the morphology of wax crystals nucleated by EVA.²⁷

One EVA acts as a nucleator rather than a growth inhibitor. This is thought to be due to the lower percentage of vinyl acetate groups, between 16 to 19 wt%, and higher molecular weight compared to a growth inhibitor EVA. The favoured action as a nucleator is suggested to be due to the long un-disrupted alkane backbones of this nucleator EVA, which can act as nucleation sites.²⁸ The EVA's higher molecular weight also give it a lower solubility, causing it to precipitate from solution before the *n*-alkanes, again providing a nucleation site. Figure 1.7 shows the change in morphology of a crystal nucleated by an EVA. It is inferred that the

needle-like morphology induced is a result of the EVA chain aligning with the long axes of the *n*-alkanes in the wax.

An EVA with a higher vinyl acetate percentage, typically between 27 to 30 wt%, does not have long, uninterrupted alkane segments to provide sites of nucleation and thus the EVA acts as a growth inhibitor. In this case, it is thought that the alkane backbone provides affinity with (and adsorbs onto) the pre-formed wax crystal face and the polar vinyl acetate groups extend out from the surface preventing further crystallisation.^{24,25}

1.5.2 Fumarate vinyl acetate copolymers (FVA)

FVA, shown in Figure 1.8, is one of a large family of comb polymers, with variations in backbone and side chain structure that have been extensively used as wax crystal modifiers.²⁹

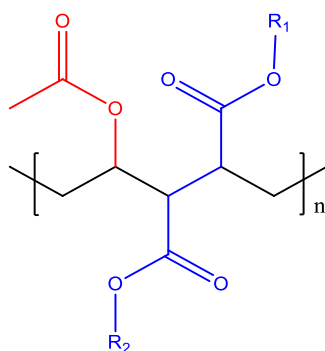


Figure 1.8: General structure of a fumarate vinyl acetate copolymer (FVA), vinyl acetate shown in red and fumarate shown in blue.

Adsorption, co-crystallisation, nucleation and improved wax solubility are the most widely accepted theoretical mechanisms proposed for the interaction of comb polymers with wax crystals, although exactly which of these is/are in action in a given system is still subject to debate.³⁰ Previous studies looking at the mechanism of FVA – wax crystal interaction have indicated that chain matching of the alkyl side chain length and that of the *n*-alkane is a key factor in achieving the van der Waals interactions needed for wax crystal modification.^{30,31}

Lewtas *et al.* measured the solubility of *n*-dotriacontane (*n*-C₃₂H₆₆) in the presence of a range of FVAs and found that FVAs with a side chain length of C₁₈ significantly increased the solubility of the alkane in *m*-xylene. A suspected possible explanation for this observation is that FVA co-crystallises with the *n*-alkane, with the two alkyl side chains of the polymer, R₁ and R₂, lying parallel to the *n*-alkanes. This suggests that chain matching between the total alkyl side chain

length (across the polymer) and the *n*-alkane is important.^{31, 32} However, molecular dynamic simulations of a poly-octadecyl acrylate comb polymer with *n*-octacosane by Duffy *et al.* showed the polymer backbone aligned along the inter-lamellar gap (Figure 1.9).³³ This could indicate that one alkyl side chain length rather than the total length of two side chains across the polymer could also affect the crystallisation.

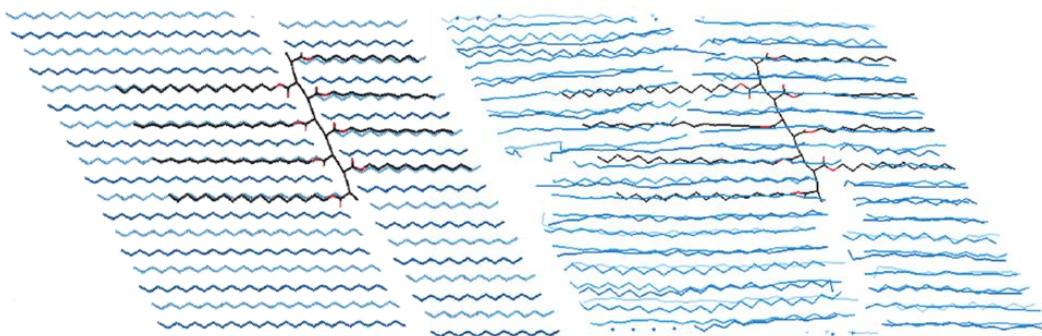


Figure 1.9: Left: Showing the adsorption of poly-octadecyl acrylate onto *n*-octacosane crystal with the backbone in the inter-lamella gap, pre-simulation. Right: Showing the disruption of the crystalline order upon addition of the polymer, post simulation.³³

Comb polymers have also been suggested as effective MDFIs for biodiesel. Wang *et al.* studied the effect of EVA, poly-methyl acrylate (PMA), poly α -olefin and polymaleic anhydride additives on biodiesel from waste cooking oil.³⁴ The results indicated that PMA had the greatest effect, retarding crystal growth and changing crystal morphology inhibiting the formation of larger crystals.

1.5.3 Wax Anti-Settling Additives

WASAs or wax crystal dispersants are used in commercial products to limit the settling or sedimentation of wax crystals by reducing the crystal size and improving the stability of the suspensions of wax crystals. The commercial Infineum WASA is OA 6399, which has an amide-ammonium salt monomeric structure derived from phthalic anhydride, shown in Figure 1.10. Other known, but less effective, WASAs include different polymeric or monomeric structures such as imides³⁵, linear amides^{36,37} and novel dimer/Gemini structures.³⁸

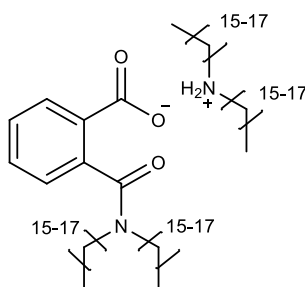


Figure 1.10: Di-hydrogenated tallow ammonium 2-(di-hydrogenated tallow carbamoyl) benzoate or OA 6399.

In comparison with other wax crystal modifiers, the mechanism of WASA action has received very little attention in the scientific literature and current knowledge is mainly sourced from industry and reported in patents. The scientific literature on WASAs is summarised below.

Two WASA modes of action have been proposed. According to Stokes' Law, which assumes perfect spheres, smaller particles should settle slower than larger ones:

$$V = \frac{2r^2\Delta\rho g}{9\eta} \quad 1.2$$

where V – Stokes velocity, r – radius of sphere, $\Delta\rho$ – difference of density between sphere and solution, g – gravitational acceleration and η – dynamic viscosity.³⁹

Firstly, WASAs reduce the wax crystal size. Whilst MDFIs typically reduce the crystal size from a few mm to around 30 μm , the addition of a WASA further reduces them to 5 – 10 μm . This improves CFPP and slow-cooling performance due to the increased filterability of the smaller crystals, even in biodiesel fuels.^{40,41} However, this decrease is not significant enough to produce the large anti-wax settling effect observed.⁴²

Secondly, the WASA could act as a wax dispersant by stabilisation of the wax crystal suspension. Aggregation and agglomeration of wax crystals would form a larger structure, which would in turn increase the sedimentation rate. The mode by which this aggregation occurs in wax is unknown, but is probably accounted for by dispersion forces, and so is the method by which WASAs prevent it. To date, experimental data has not definitively shown that the prevention of crystal aggregation occurs.⁴²

Marie *et al.*⁴² showed the location of EVA and WASA in a wax crystal from a model diesel, rapidly (unrealistically) cooled to below its CP (-7 °C), to produce a signature traceable peak by IR spectroscopy using the ester peaks at 1738 cm^{-1} and 1635 cm^{-1} for the EVA and WASA respectively. The crystals were found to be EVA and WASA enriched compared to the solution. However, when the crystals were washed with ethyl benzene, removing their outermost layer, the amount of WASA detected dramatically decreased while the amount of EVA stayed constant. This shows that, under these conditions, the EVA is homogeneously dispersed

throughout the crystals supporting the theory of its role as a co-crystallising nucleator or growth inhibitor, and that under these conditions WASA is adsorbed onto (and co-crystallises with) the surface of the crystals, lowering their interfacial energy.

The settling rate of the EVA and WASA-doped model diesel was also measured using a specially designed turbidimeter. Large differences in settling rate between the different WASAs were observed even though they produced similar sized crystals. The observed settling rate showed with no relation to the mean crystal sizes. The latency time (time before any settling occurred) varied between WASAs and doping amount. A long latency time reflects a slow aggregation rate or a fragile network of weakly flocculated particles, which prevents sedimentation. This supports the theory that WASAs act as wax dispersants preventing aggregation and thus sedimentation.

Yu-hui and Ben-Xian used a quantitative structure-activity relationship (QSAR) to evaluate the structures of WASAs.^{27,43} They typically have two opposing sides; one contains several *n*-alkyl chains of a similar length to the *n*-alkanes, and the other contains a polar group. The QSAR model showed the factors regulating the flow-improving activity of the WASA are mainly of a geometric or morphological nature. Their study suggested that effective WASA molecules have a higher percentage of apolar surface area from the long alkyl chains and a large polar region, and thus a large dipole across the molecule. Molecular mass and surface area may also be important; this can be rationalised by considering the surface interaction of WASAs and crystals. The long apolar chains can co-crystallise with the wax thus securing the WASA to the surface of the wax crystal, whereas the polar group can act as a dispersant (Figure 1.11). The contribution of electrostatic repulsions has been put forward as an action by which the polar groups can prevent aggregation, but there has been no convincing evidence to date.⁴² However, additives imparting charge to wax crystals has been reported previously.⁴⁴

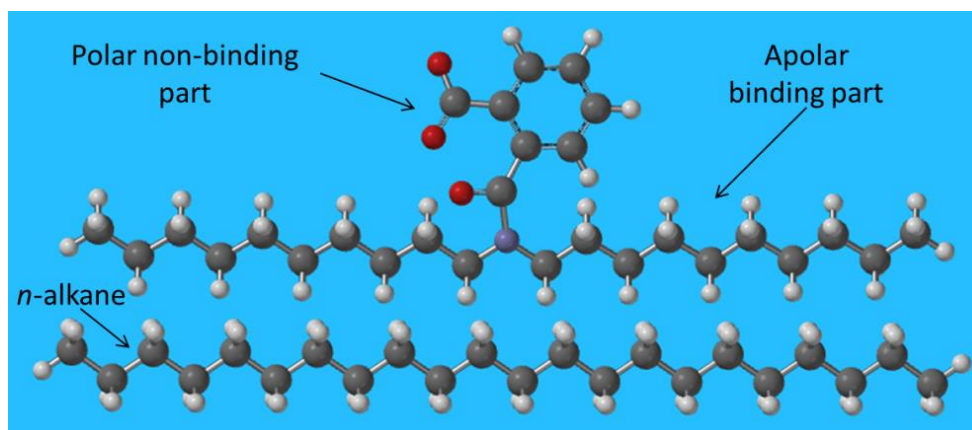


Figure 1.11: Model of a WASA-like molecule interaction with *n*-alkane representing a wax crystal surface. (Grey – carbon, white – hydrogen, purple – nitrogen and red – oxygen).

WASA crystal modification is most effective in the presence of MDFIs, so the two are combined into a single wax anti-settling flow improver (WAFI) package for optimal results. Maithufi has suggested that the WASA interacts directly with the polymeric MDFI additive rather than the fuel.³⁸ A more probable theory, as evidenced by the studies discussed above, is that the MDFIs (for example EVA) co-crystallise and nucleate the wax crystals, then subsequently WASAs interact with the wax surface. The EVA needle-like modification causes a larger surface area of fast-growing crystal faces, which in turn means the WASA can be adsorbed onto these faces more efficiently.²⁷ Crystals formed in the presence of WASAs tend to be less needle-like and more compact, suggesting that all crystal surfaces have been affected.⁴⁵

Another factor affecting the efficiency of WASAs is matching the size and shape of the molecule with the wax crystal lattice. Termed ‘molecular trickery’ by Clydesdale and Roberts, tailoring additives to fit into the lattice spacing of the crystal by mimicking the true crystal components is a powerful technique.⁴⁶ OA 6399 was created by Lewtas for Exxon in 1978 taking advantage of this technique. Using crystallographic data and molecular modelling it was found that an ideal WASA molecule, able to co-crystallise with crystal planes, needed: two substituent groups 4.5 – 5.0 Å apart to match the *n*-alkanes in the (001) plane intersecting the (11x) plane; and a dihedral angle between the local symmetry planes of 75° – 90° matching the direction of the *n*-alkanes in the (110) direction. This allows the molecule to ‘dock’ into two vacant lattice sites. OA 6399 was found to provide this using substituent alkyl groups with a matching chain length to that of the *n*-alkanes.⁴⁷

The mechanism by which the WASA may disperse the wax crystals remains unknown. This overall aim of the work reported in this study is to elucidate this action. To better understand the action of additives such as WASAs, it is first important to understand the fundamental science of wax crystals in suspension acting as a colloid.

1.6 Colloid stability

Colloids are a multiphase system distinguished by one phase dispersed in a distinct continuous phase. The length scale of the dispersed phase is typically between nanometres to microns in size. Colloids are ubiquitous in nature, industry and modern life. Examples include mayonnaise (an oil in vinegar emulsion), paint (pigment particles dispersed in liquid) and mist (water droplets dispersed in air).

Colloidal particles are only kinetically, not thermodynamically, stable, since a solid mass not dispersed in solution would be lower in energy. If the density between the particles and solution is similar, then colloid particles are generally small enough to be suspended in the fluid by thermal (Brownian) motion. A dispersion of colloidal particles will aggregate due to van der Waals attractions. To counter this many systems rely on an energetic barrier provided by electrostatic or steric interactions for stability. Interparticle interactions between colloid particles can be tuned from strongly repulsive to attractive by carefully controlling their interfacial properties.

In aqueous systems, Derjaguin-Landau-Verwey and Overbeek (DLVO) theory describes the force between charged colloids interacting through a liquid medium. It combines the effect of the van der Waals attraction and electrostatic repulsion. The stability of a colloid depends on there being a maximum in the interaction energy that is large compared with $k_B T$.

1.6.1 Attractive forces

1.6.1.1 Van der Waals interactions

Three effects contribute to van der Waals attractive forces; Keesom (dipole – dipole), Debye (dipole – induced dipole) and London (induced dipole – induced dipole). A permanent dipole will attract similar dipoles and they will align. Dipoles can also induce a dipole in a nearby neutral atom or molecule and cause an attraction. All molecules have fluctuating dipoles due to the motion of electrons, it

is more favourable for adjacent molecules to fluctuate in unison and have aligned dipoles. Colloidal particles are large assemblies of atoms and hence these van der Waals cause attractions in colloids. The attractive potential energy due to London dispersion interactions can be calculated as:

$$V_A = -\frac{A}{12} \left[\frac{1}{x(x+2)} + \frac{1}{(x+1)^2} + 2 \ln \frac{x(x+2)}{(x+1)^2} \right], \text{ with } x = \frac{h}{2r} \quad 1.3$$

where A – Hamaker constant, r – particle radius and h – distance of separation. If $h \ll 2r$ this reduces to:

$$V_A = -\frac{Ar}{12h} \quad 1.4$$

The Hamaker constants are in the range of 10^{-20} J but vary depending on the electronic polarisability and density of the colloid and on the continuous phase the colloid is in:⁴⁸

$$A = \left(\sqrt{A_{\text{colloid}}} - \sqrt{A_{\text{continuous phase}}} \right)^2 \quad 1.5$$

Hydrogen bonding is not strictly a van der Waals force but will still be discussed here. Classical H-bonding is between $A - H \cdots B$ where A and B are electronegative elements typically nitrogen, oxygen and fluorine. Non-classical H-bonding has also been seen between aromatic rings and hydrogen.⁴⁹ Self-assembly of colloids using hydrogen bonding has been observed.⁵⁰

1.6.1.2 Depletion interaction

Depletion forces are known to play many pivotal roles in colloid science⁵¹ through to cell structure⁵². Depletion interactions occur when small non-absorbing species in solution such as molecules, polymers or small particles, induce attractions between larger colloidal particles. Depletion interactions were first suggested as a mechanism for reversible flocculation observed in colloid–polymer mixtures by Asakura and Oosawa.⁵³ The interaction occurs as the non-absorbing species is excluded from the surface of the large colloid. As the large colloids approach each other these excluded volumes overlap creating a depletion zone for the small species and thus a concentration gradient between the depletion zone and the bulk solution. This in turn generates an osmotic pressure which attracts the large colloids together. Figure 1.12 shows a diagram of this interaction. The strength of the attraction depends on the concentration of the small species, while the range of the attraction is set by the size of the small entity and is longer range than van der Waals forces.⁴⁸

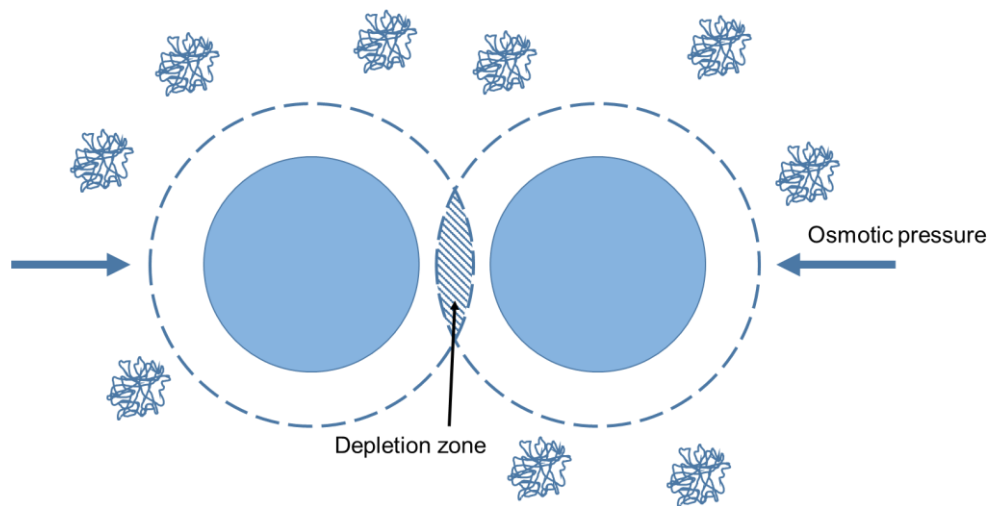


Figure 1.12: Diagram depicting the depletion interaction.

1.6.1.3 Bridging Interactions

At low surface coverage, adsorbing polymers may adsorb to two colloids *via* polymer loops and tails, bridging the gap between the particles and causing bridging flocculation. This interaction can be attractive under better than theta solvent conditions.⁴⁸ Ruehrwein and Ward first proposed the basic principle of bridging flocculation in 1952, with a single polymer chain bridging between two or more particles.⁵⁴ Controlling the aggregate structure formed during a bridging flocculation is non-trivial; the polymer chemistry, charge, dosage and the particle surface charge all play a factor. The dimensions of the polymer also play a role and are dependent on the solvent affinity for the polymer chain segments. A high solvent affinity will lead to coil expansion whereas, a poor affinity will cause collapse.⁵⁵

1.6.2 Repulsive forces

1.6.2.1 Steric stabilisation

A layer of surfactant or polymer absorbed to the surface of the colloid physically prevents the colloids from meeting, shown in Figure 1.13. The strength and range of the repulsion depends on the thickness and density of the layer and the Flory-Huggins parameter, which represents the interaction of the absorbed layer with the solution. Effective stabilisation is achieved by a high surface coverage and a strongly absorbed and solvated molecule.⁵⁶

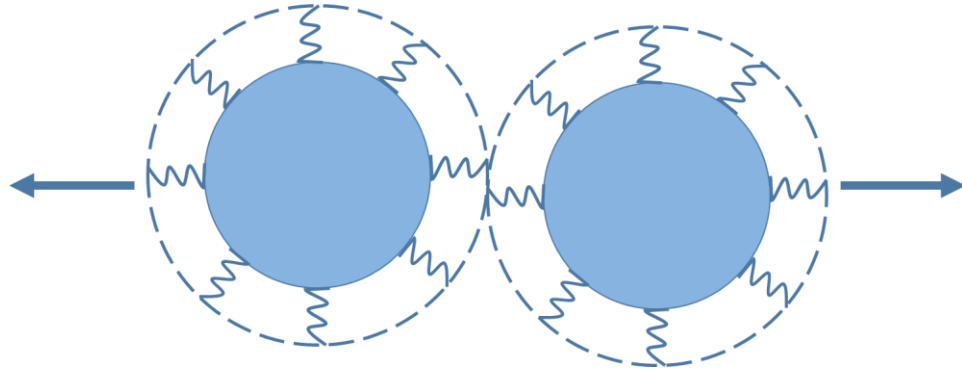


Figure 1.13: Diagram depicting steric stabilisation.

1.6.2.2 Electrostatic repulsion

To maintain overall charge neutrality a charged surface requires an excess of counter charges in solution, as ions or in micelles. The interaction of the surface and solution charges is called an electrical double layer. The excess of counter-charges is attracted to the charged surface. However, a large concentration of charges is entropically unfavourable thus a thermodynamic equilibrium distribution of the charges is reached.

The distribution of the charges can be modelled by the Stern model (a combination of the Helmholtz and Gouy-Chapman models) depicted in Figure 1.14.^{48,57} This shows a decreasing concentration of cations existing in two distinct regions; the Stern layer (an inner layer of cations attached to the charged surface) and the diffuse layer (which includes the inner and outer Helmholtz layers closest to the Stern Layer). The shear plane is a boundary between the dispersion medium and stationary layer attached to the surface at which the electric potential is equal to the zeta-potential. The zeta-potential is often used as a measure of the electrical charge as it is difficult to measure the absolute charge of a charged surface

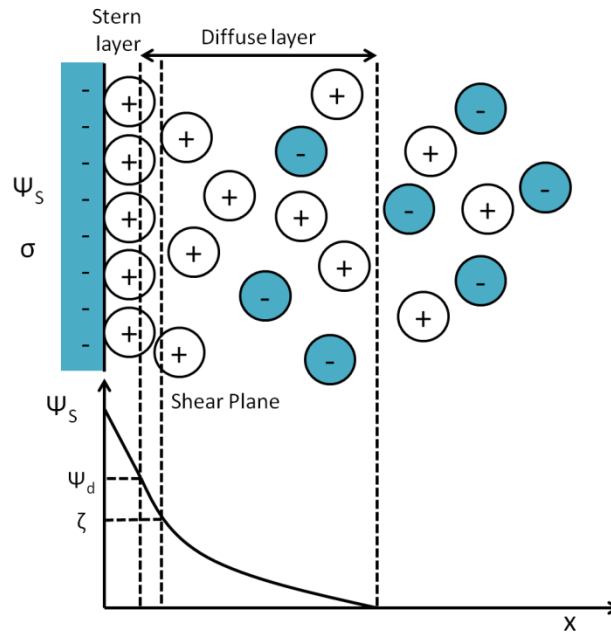


Figure 1.14: Schematic of the ions near the charged colloid in the Stern model. Ψ_s – potential at the colloid surface, σ – surface charge density, Ψ_d – potential at the outer Helmholtz layer and ζ – zeta potential at shear plane.⁵⁷

Electrical double layers stabilise colloids with respect to agglomeration due to the entropic penalty of confining these counter-charges into the space between the colloids as they interact. This causes a repulsion arising from the resulting osmotic pressure. The Debye length is the distance over which two charged surfaces interact through their electrical double layers. The larger the particle the lower the electrical charge needed for stable dispersion.⁴⁸

In non-aqueous media such as diesel the measurement of electrostatic repulsion is different to aqueous media. A key difference between aqueous and non-aqueous liquids is the ability of the liquid to generate an internal electric field that opposes an applied, external field, known as the dielectric constant. The dielectric constant (ϵ) is roughly 80.4 for water and 2 for hydrocarbon solutions such as diesel. Diesel lies in the apolar range ($\epsilon \leq 5$) where electrostatic stabilisation may be problematic due to the instability of formal charges in solution.⁵⁸ The distance needed to electrostatically isolate the two ions of common salt, NaCl, in a solution is known as the Bjerrum length, λ_B (the distance at which the columbic attraction between the ions equals their thermal energy, kT):

$$\lambda_B = \frac{q^2}{4\pi\epsilon\epsilon_0 kT} \quad 1.6$$

where q – charge on ions, ϵ_0 – permittivity of free space and ϵ – dielectric constant for the given medium. At room temperature $\lambda_B = 0.7$ nm in water and 28 nm in

hydrocarbon solutions. This means that to provide charge separation of salt the hydrocarbons would require a 14 nm thick solvation sphere surrounding each ion. Thus, a large amount of energy is required to dissociate the ions and they can only remain dissociated in low dielectric media if they are large or contained by a large structure. There currently exists no successful quantitative theory to describe the origins and interactions of charge in non-polar systems, comparable to that of DLVO theory for aqueous systems. Such an understanding is needed to fully understand and exploit charge in non-polar systems.⁵⁹

Recently, non-aqueous colloid stabilisation has been utilised in the petroleum industry in the dispersion of soot particles. Without dispersion, soot particles produced in the combustion process agglomerate into 30 nm structures. This causes engine wear problems and oil thickening, leading to oil circulation problems.⁶⁰ Evidence suggests that small soot particles are stabilised *via* electrostatic stabilisation using polymeric dispersant additives to disperse the counter ions.⁶¹ This sets a precedent for electrostatic stabilisation in these systems and some of the same experimental techniques, such as electrophoresis, will be used in this study.

1.7 Colloidal arrested states

Colloidal arrested states are a state in which a material dispersion does not flow over practical timescales and has properties such as a yield-stress, like a solid. Many household, natural and industrially important colloidal materials are solid-like and their behaviour has profound implications for various industrial applications. Due to the ability to control the size and interactions of the colloidal particles the states they form can also be used as useful model systems for more traditional atomic or molecular solids.

The two most common arrested colloidal states are gels and glasses. Both are long-range, disordered solids with large viscosities, finite elastic modulus and little particle diffusion. They are usually thermodynamically out of equilibrium and thus gradually structurally change or 'age' over time to lower their free energy. The lifetime of arrested states is dependent on the interparticle interactions and bond lifetimes. A detailed review by Zaccarelli outlines many different routes to gelation.⁶²

1.7.1 Colloidal gel

Colloidal gels can form in dilute systems at lower volume fractions, Φ_v . Gels are formed due to short-range but strong attractive interactions. Particles diffusing in solution aggregate into clusters, due to these strong attractive forces. Gelation occurs when these clusters grow large enough to aggregate into large scale percolated network-like structures forming the gel. The clusters have a fractal structure with a small number of particles occupying a large volume of space. A fractal structure can be characterised by its fractal dimension, d_f , which is the power law exponent that relates the mass, M , to the length scale, R , of the structure such that $M \propto R^{d_f}$.

There are broadly speaking two types of gel; diffusion-limited cluster aggregation (DLCA) and reaction-limited cluster aggregation (RLCA). DLCA occurs when diffusion-controlled collision of the particles causes strong bond formation, so the diffusion of the particles is the only factor causing the gel structure. This results in a more open network with a small d_f of 1.8. RLCA occurs when there is an energy barrier to bond formation which must first be overcome. Thus, multiple collisions must occur for an interparticle bond to form. This results in a more compact gel with a higher d_f of around 2.1 in the dilute limit.⁶³

1.7.2 Colloidal glass

Conversely to gels, colloidal glasses form as the volume fraction, Φ_v , of the particles increase. The particles interact by volume exclusion, so as the Φ_v increases the structural relaxation slows dramatically, causing structural arrest while maintaining the original liquid state disorder. Glasses can be attributed to the effect of either dominant repulsive (excluded-volume or electrostatic) or dominant attractive (depletion) interactions. For a simple case of monodispersed spherical particles in suspension, below $\Phi_v < 0.494$ there exists a fluid state and beyond $\Phi_v > 0.545$ a crystalline state exists. However, if Φ_v is increased quickly thus not allowing the formation of crystalline nuclei, beyond $\Phi_v > 0.58$ the particles can be considered trapped by their neighbours. This concentration is associated with the colloidal glass transition. This transition and its associated rheological response have been well described using mode-coupling theory.⁶⁴

1.7.3 Diesel gelation

Examples of colloidal gels can be seen in the gelation of diesel and crude oil in deep sea pipe lines by the large wax crystals.⁶⁵ This colloidal gel can require as

little as 2% solid wax to form.⁶⁶ The gels formed have been studied by rheology^{66,67}, scattering techniques⁶⁸ and spectroscopy.⁶⁹

Paso *et.al.* showed how *n*-alkane polydispersity facilitates mechanical gelling in a mineral oil and *n*-alkane system. Above the crystallisation temperature of the alkanes the system gives a typical Newtonian response. After an initial nucleation event, the presence of wax crystals causes an increase in the viscosity, followed by the formation of random interacting networks among the growing crystals. This imparts a solid-like mechanical response, shown by an increase in the elastic storage modulus, G' . This is thought to be due to a gelation occurring by the growing wax crystals interlocking to form a volume-spanning crystal network which entrains the remaining liquid oil.⁷⁰

Vignati *et.al.* used small angle light scattering on a model diesel system to obtain a d_f for the gel *via* the Fisher–Burford expression for the structure factor of a fractal colloidal gel. This technique gave a d_f of 1.8 ± 0.1 suggesting a diffusion-limited cluster aggregation.⁶⁸

1.8 Thermodynamic models

During this work two thermodynamic models were used and will be introduced here. The eutectic model was used to ascertain whether the waxy alkanes in the model diesel co-crystallise with each other and with the WASA. It also gives insight into determining the extent to which the decrease in crystallisation temperature upon addition of WASA is due to the WASA action or is simply a melting point depression due to mixing. The van't Hoff solubility model was used to compare the solubility of WASA, C₂₂ FVA and *n*-alkanes in dodecane to help ascertain the mechanism of the additives action.

1.8.1 Eutectic model

These substances with eutectic behaviour ideally mix in the liquid phase but do not mix in the solid phase. A eutectic mixture is a mixture of substances having the lowest freezing point of all possible mixtures of the substances. The melting temperature at this special combination is called the eutectic temperature, T_e .⁷¹ A basic phase diagram describing a eutectic mixture is depicted in Figure 1.15.

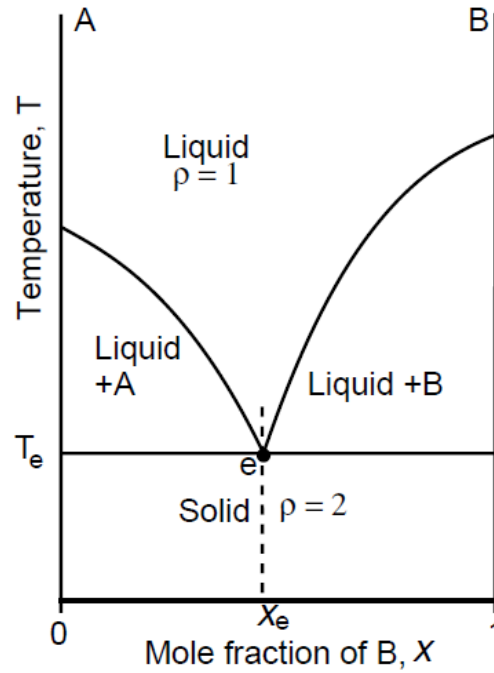


Figure 1.15: Solid-Liquid temperature mole fraction phase diagram for a binary system.⁷¹

To calculate the freezing point of two substances with eutectic behaviour, we must start with the chemical potentials of each component. At the freezing point the chemical potentials of the component in the liquid phase is equal to the solid phase. The components in the solid state do not mix and thus the chemical potential of each component is the same as the chemical potential of the pure solid:

$$\mu_a^*(s) = \mu_a^*(l) + R_g T_{m,a} \ln x_a \quad 1.7$$

Where x_a is the mole fraction of A.

$$\mu_{a,s}^\circ(l) - \mu_{a,s}^\circ(s) = R_g T_{m,a} \ln x_a \quad 1.8$$

$$\frac{1}{R_g} \frac{d(\Delta G(s \rightarrow l))}{dT} = \frac{d}{dT} (\ln x_a) \quad 1.9$$

Using the Gibbs-Helmholtz equation then integral, we have:

$$- \int_{T_{m,a}}^T \left(\frac{\Delta H_a}{T^2} \right) dT = R_g \int_0^{\ln x_a} d(\ln x_a) \quad 1.10$$

On integrals we have the liquidus line in the phase diagram:

$$T = \frac{\Delta H_a^\circ T_{m,a}}{\Delta H_a^\circ - R_g T_{m,a} \ln x_a} \quad 1.11$$

This model will be used to determine the eutectic temperature or freezing point depression in *n*-alkane mixtures compared to crystallisation temperature decrease of additives.

1.8.2 Van't Hoff solubility model

For dilute systems, the van't Hoff equation has been shown to model the solubility of a solute. This expression is derived from the general expression of solid-liquid equilibrium assuming that the specific heat capacity can be neglected.

Combining the Gibbs free energy equation and the Gibbs free energy isotherm equation gives the van't Hoff equation:

$$\Delta G = \Delta H - T\Delta S \quad 1.12$$

$$\Delta G = -RT \ln x \quad 1.13$$

Therefore:

$$\ln x = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad 1.14$$

Where x – mole fraction of the solute in the solution, T – solution temperature, ΔH (J/mol) – molar enthalpy of crystallisation, ΔS – molar entropy of crystallisation and R – gas constant.^{12,72}

The entropy and enthalpy of crystallisation of the solute can be found by heating and cooling different concentrations of the solute at different ramp rates, then extrapolating to 0 °C.min⁻¹ for the different concentrations and plotting $\ln(1/x)$ vs $1/T$ to gain the enthalpy and entropy of crystallisation. An endothermic reaction would give a negative slope as $\Delta H > 0$ whereas an exothermic reaction would give a positive slope as $\Delta H < 0$. For most substances dissolution is an endothermic process and crystallization an exothermic process.

1.9 Thesis outline

The aim of this thesis is to elucidate the mechanism of wax anti-settling additives. The previous section outlined background literature and introduced the industrial need for such additives, as well as some of the theories and principles relevant to the work. Chapter two describes the materials purchased and synthesised and the experimental methods and techniques employed in this research. Chapters three to five detail the results and analysis of experiments undertaken. Chapter three deals with the development and testing of a model diesel used throughout this

work, the effect of additives upon that model diesel and the location of the WASA within the model diesel using a variety of techniques. Chapter four consists of electrophoresis and rheological tests to reveal how the anti-settling effect occurs. Chapter five presents the small angle neutron scattering data and explores what this information tells us about the structure of the WASA. This experimental data will be brought together in discussion in chapter six, where each results chapter will be discussed in turn. Chapter seven brings the discussions together and makes final conclusions as to the mechanism of the WASA and future work.

2 Materials and Methods

2.1 Materials

2.1.1 Purchased Solvents and *n*-Alkanes

Solvents (ReagentPlus® grade Dodecane, Toluene and Heptane) and *n*-alkanes (see Table 2.1) were purchased from Sigma Aldrich and used without further purification.

Table 2.1: Chemical name, formula and purity of *n*-alkane purchased from Sigma Aldrich

Name	Formula	Purity
Eicosane	C ₂₀ H ₄₂	99%
Tetracosane	C ₂₄ H ₅₀	99%
Octacosane	C ₂₈ H ₅₈	99%
Dotriacontane	C ₃₂ H ₆₆	97%

2.1.2 Industrial Additives

2.1.2.1 Wax Anti-Settling Additive

The WASA (*di*-hydrogenated tallow ammonium 2-(*di*-hydrogenated tallow carbamoyl) benzoate) was synthesised at Infineum and used without further purification. The synthesis used phthalic anhydride which was purchased from Sigma Aldrich and was used without further purification. Care was taken to use fresh reagent due to old phthalic anhydride undergoing hydrolysis with water vapour. Armeen 2HT (*di*-hydrogenated tallow amine) was supplied from Infineum via AkzoNobel and used without further purification.

Phthalic anhydride (4 g, 27.0 mmol) and Armeen 2HT (25.2g, 54.0 mmol) were dissolved in toluene (200 ml) and placed in a round bottom flask with a magnetic stirrer. A condenser, with a septum and nitrogen in and out needles, were fitted and a nitrogen blanket applied. The solution was stirred at 60 °C for an hour. Excess toluene solvent was removed under vacuum. WASA (29.11 g, 25.6 mmol, 95 %) was isolated as a cream-coloured powder. The synthetic scheme is shown in Figure 2.1.

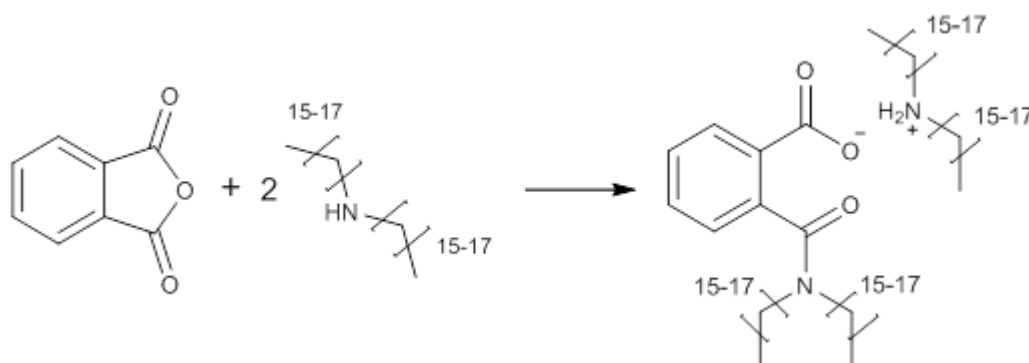


Figure 2.1: Synthetic scheme for WASA.

FT-IR (neat) $\nu_{\max}$ cm^{-1} ; 2956 – 2850 (m, aryl and alkyl CH stretch), 1634 (w, Amide C=O stretch) 1468 (w, alkyl CH) 1377 (w, alkyl CH) 728 – 507 (s, fingerprint region including aromatic CH), see Figure 2.2.

$^1\text{H-NMR}$ (300 MHz, CDCl_3) δ / ppm; 7.99 – 7.14 (4H, m, Ar-H), 3.00 (4H, broad s, $\alpha\text{-CH}_2$ amide), 2.80 (4H, t, $\alpha\text{-CH}_2$ amine salt), 1.56 (8H, m, $\beta\text{-CH}_2$ amine salt and amide), 1.31 – 1.17 (112H, m, $(\text{CH}_2)_n$), 0.89 (12H, t, CH_3), see Figure 2.6.

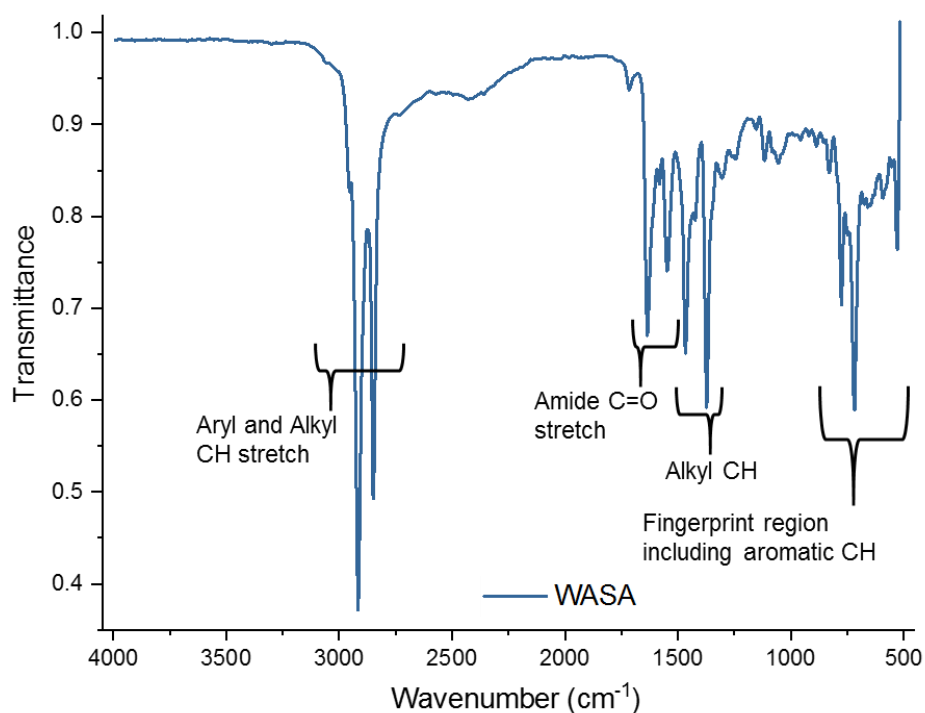


Figure 2.2: FT-IR spectrum of WASA

2.1.2.2 Polymers

Two commercial Infineum FVAs with different side chain lengths ($\text{C}_{14/16}$ and C_{22}) were used without further purification. The fumarate monomers used in the copolymerisation are synthesised from a range of alcohols, thus giving the

different average side chain lengths in the FVA. A commercial Infineum nucleator EVA was also used without further purification.

2.1.3 Alternative Additives

Ionic liquids $PC_4.Cl^-$ and $[BMiM][NtF_2]$ were kept in an airtight container and used without further purification (Figure 2.3). AOT, Dioctyl sulfosuccinate sodium salt, was purchased from Sigma Aldrich and used without further purification.

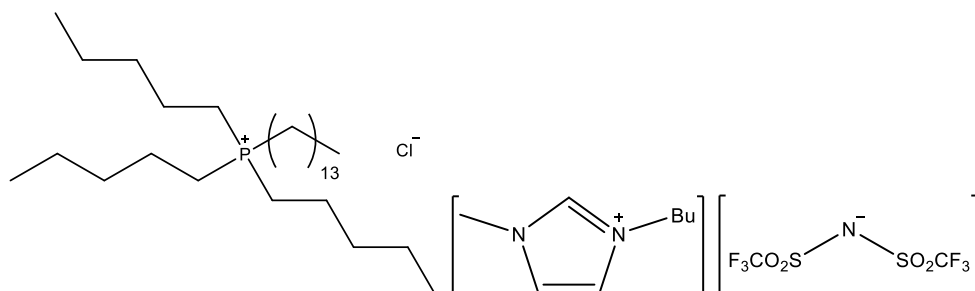


Figure 2.3: Structures of ionic liquids $PC_4.Cl^-$ and $[BMiM][NtF_2]$

Organic salt, Tetrabutylammonium bromide, was purchased from Sigma Aldrich and used without further purification (Figure 2.4).

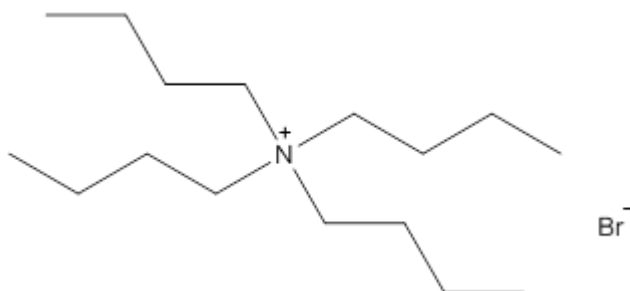


Figure 2.4: Structure of organic salt Tetrabutylammonium bromide

2.1.4 Deuterated Materials

Deuterated waxy *n*-alkanes, dodecane and reagents were purchased from a range of suppliers depending on availability and cost. All were used without further purification and kept in airtight containers to slow D/H exchange. The purity and supplier information of deuterated reagents are listed in Table 2.2 for the NIST neutron beam time and in Table 2.3 for the ISIS neutron beam time.

Table 2.2: Purity and supplier of deuterated reagents for NIST, Washington beam time

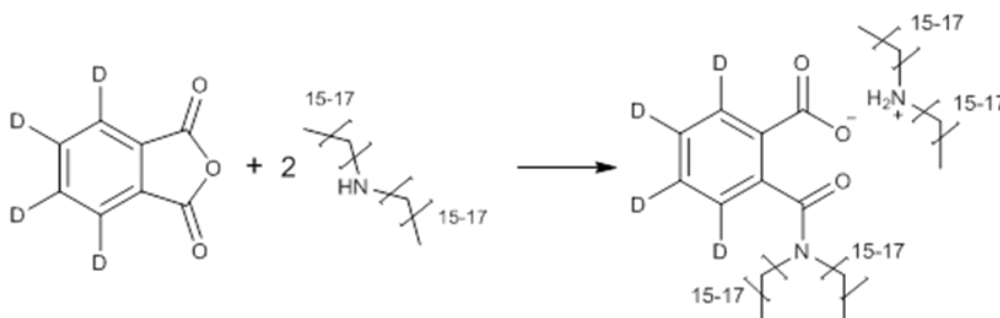
Reagents	Purity	Supplier
Eicosane	98%	CK Isotopes
Tetracosane	98%	CK Isotopes
Octacosane	98%	CK Isotopes
Dotriacontane	98%	CK Isotopes
Dodecane	98%	CK Isotopes
Phthalic anhydride	98%	CK Isotopes

Table 2.3: Purity and supplier of deuterated reagents for ISIS, Oxford beam time

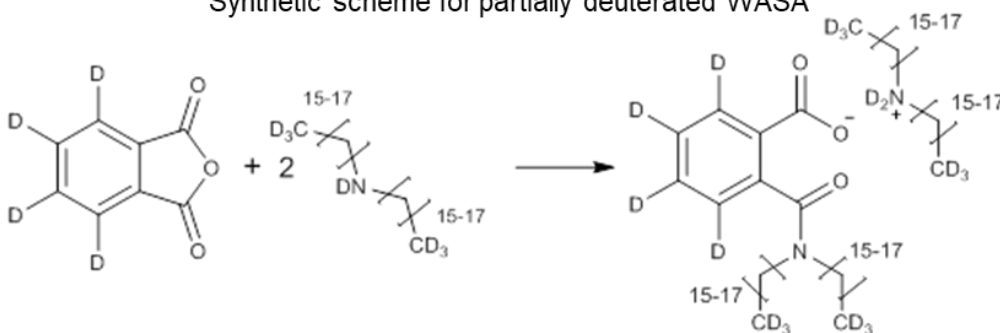
Reagents	Purity	Supplier
Eicosane	98%	CK Isotopes
Tetracosane	98%	CK Isotopes
Octacosane	98%	Qmx Laboratories
Dotriacontane	98%	CK Isotopes (from NIST run)
Dodecane	98%	CK Isotopes
Phthalic anhydride	98%	CK Isotopes

2.1.4.1 Synthesis of deuterated materials

Partial and ‘fully’ deuterated WASA were synthesised using the same method described in 2.1.2. Partially deuterated WASA (Dp-WASA) was made using deuterated phthalic anhydride, while ‘fully’ deuterated WASA (D-WASA) was made using deuterated phthalic anhydride and partially deuterated Armeen 2HT. Both synthetic schemes and reaction set up can be seen in Figure 2.5.



Synthetic scheme for partially deuterated WASA



Synthetic scheme for deuterated WASA



Synthesis set up for (deuterated) WASA

Figure 2.5: Synthetic schemes and set up for the synthesis of deuterated WASA.

The Armeen 2HT was deuterated by Colin Willis at Infineum. He was able to achieve 100% deuteration of the amine, 50% deuteration of the terminal CH_3 and 13% deuteration of the CH_2 groups. This provided sufficient contrast for SANS. The method for deuteration of Armeen 2HT was adapted from Yamada *et.al.*⁷³ A 0.3L Parr autoclave was charged with a rhodium and platinum on carbon catalyst, deuterium oxide and Armeen 2HT. The bomb was flushed with nitrogen, pressurised with hydrogen to approximately 2 – 3 bar and heated to 80 °C. The reaction was left stirring for 3 days and then flushed with nitrogen to leave

overnight. The mixture was washed out of the autoclave with heptane and deionised water and filtered through celite using a Hartley funnel to remove the catalyst. The aqueous layer was removed and the remaining product dried using magnesium sulphate, filtered and the heptane removed *via* rotary evaporation.

The amounts of reagent and yields for the deuterated versions of WASA can be found in Table 2.4. Figure 2.6 shows the NMR spectra of the WASA, partially deuterated and deuterated WASA demonstrating that the deuteration was a success.

Table 2.4: Amounts of reagent and yields for the synthesis of the deuterated versions of WASA

		D-WASA	Partial D-WASA
D-Phthalic anhydride	g	0.36	0.64
	n (mmol)	2.35	4.22
Armeen 2HT	g	-	3.93
	n (mmol)	-	8.44
D-Armeen 2HT	g	2.23	-
	n (mmol)	4.70	-
Product	g	2.35	4.13
	n (mmol)	2.13	3.81
	Yield (%)	91	90

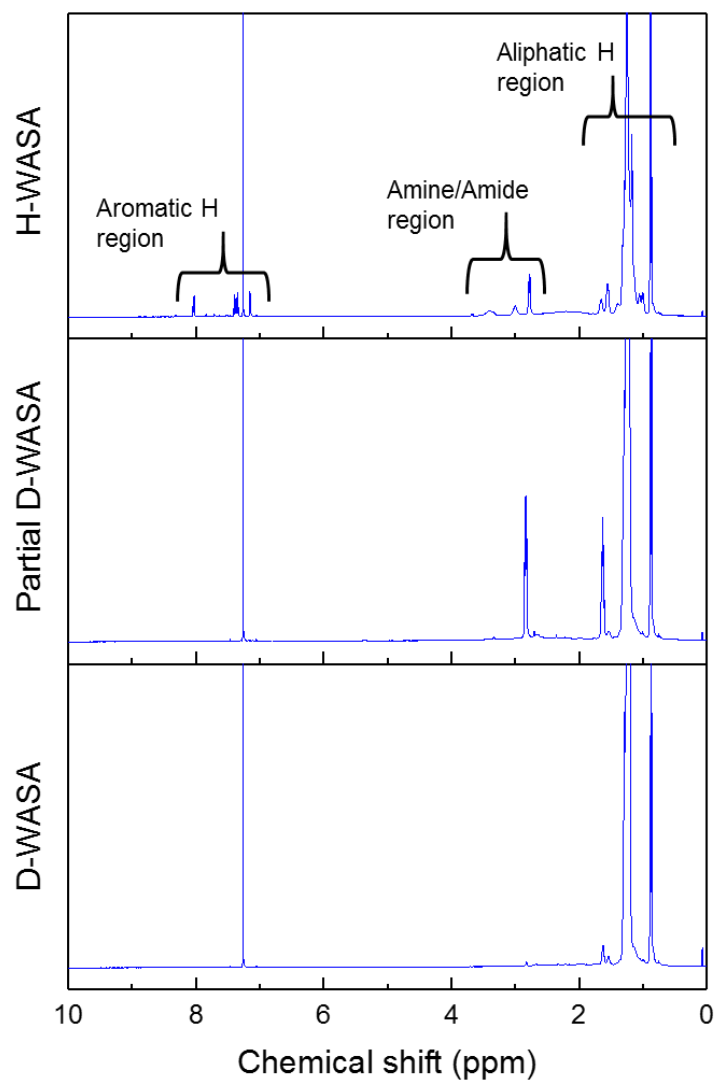


Figure 2.6: ^1H NMR spectrum of WASA and deuterated WASA

2.2 Methods and protocols

2.2.1 Model Diesel Sample Preparation

A model diesel with room temperature crystallisation properties was developed. It comprised of dodecane (the solvent) and a certain total weight percent (wt%) of single or multiple of long chain *n*-alkanes (the wax). The most commonly used model diesel was equal amounts of eicosane, tetracosane, octacosane and dotriacontane to make 10 wt% in dodecane, for example see Table 2.5.

*Table 2.5: Showing example amounts of *n*-alkanes and dodecane used to make model diesel*

Eicosane (g)	Tetracosane (g)	Octacosane (g)	Dotriacontane (g)	Dodecane (g)
2	2	2	2	72

The mixture was fully homogenised and any thermal history erased by heating to 60 °C for at least an hour and then mixing with a vortex mixer for 10 seconds. The sample was then left to cool and re-crystallise overnight. All observations were taken after the sample was homogenised and cooled.

2.2.2 Additive Doping

The model diesel was doped with additives by direct weighing or if the amount was too small *via* 10 wt% additive solutions in dodecane. These were prepared by dissolving 0.01 g of the additive in 1 g of dodecane, heating to 60 °C for an hour then mixing *via* a vortex mixer. This was then doped into the model diesel. The same procedure shown above was used to homogenise and re-crystallise the samples.

2.2.3 Optical Microscope

Wax crystal pictures were taken on a Lecia OME Optical Microscope fitted with a digital camera. Samples were pipetted onto a microscope slide. Sizes of crystals were measured by analysing 100 crystals using the microscope software.

2.2.4 Differential Scanning Calorimetry

2.2.4.1 Theory

Differential scanning calorimetry (DSC) is one of the main analytical techniques used to quantitatively show the effects of additives on wax crystallisation temperature.^{74–76} It measures the difference in heat flow between a sample pan and an inert reference pan as a function of time and temperature. The pan temperature is calculated using the weight and resistance of the pan and thermal

conductivity of purge gas. The actual sample temperature is never directly measured. As DSC is performed at a constant pressure, the heat flow is equivalent to change in enthalpy. Plotting heat flow versus temperature produces a thermogram as shown in Figure 2.7.

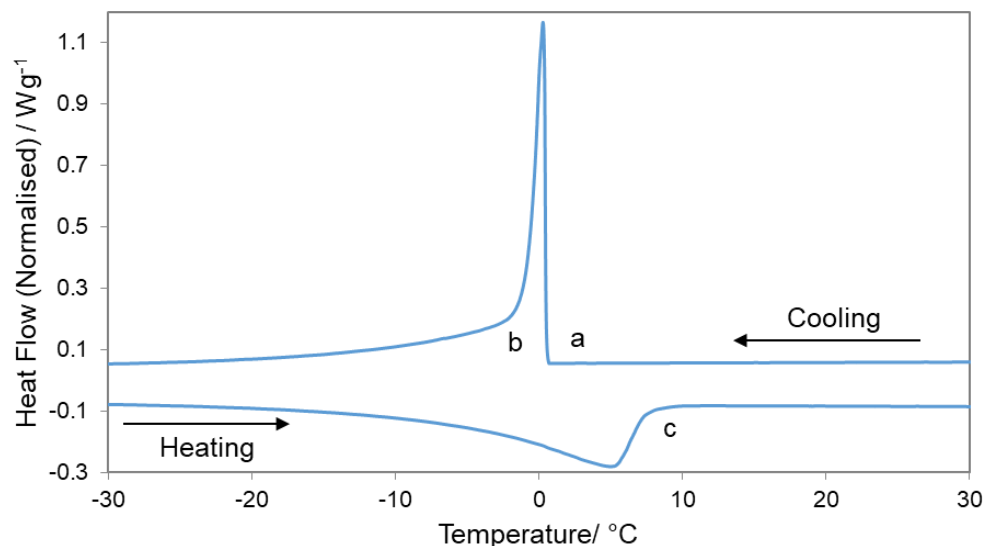


Figure 2.7: A typical diesel fuel DSC trace. The top curve is the exothermic curve showing the crystallisation properties of the sample as it is cooled. The bottom curve is the endothermic curve showing the dissolution properties of the sample as it is heated. a) Onset of crystallisation, T_c , b) Area under the curve, ΔH_{cry} , c) End of dissolution, T_d the difference between onset and end gives the metastable zone (MSZ) width.

The crystallisation temperature, T_c , is dependent upon the cooling rate, as crystallisation is a kinetic process. The rate independent T_c would only be found if the temperature ramp rate was zero (in practice, this can be done by taking measurements at different cooling rates and extrapolating to zero). The value of T_c was taken to be the temperature at the intercept of the extrapolated baseline and the steepest part of the trace on the crystallisation peak (point a on Figure 2.7). The melting temperature, T_m , was taken to be the temperature at the end of the melting peak (point c on Figure 2.7). Faster cooling rates lead to a lower T_c , faster growth rates and imperfect crystals, while slower cooling rates give a higher T_c , slower growth rates and more perfect crystals.⁷⁷

2.2.4.2 Method

DSC was performed with various heating and cooling procedures using an indium calibrated Perkin 1 DSC. A weighed ($\sim 5 \mu\text{l}$) sample of model diesel, was tested in a pre-weighed pan together with a reference pan. A typical testing procedure is shown in Table 2.6, temperatures and ramp rates were changed depending on the sample.

Table 2.6: Typical DSC testing procedure

Equilibrate at 60 °C for 5 minutes
Ramp at 2°C min ⁻¹ to -10 °C
Equilibrate at -10 °C for 1 minute
Ramp at 2 °C min ⁻¹ to 60 °C
Equilibrate at 60 °C for 1 minute
Repeat cycle then end

All data were taken from the second cycle. A ramp rate of 2 °C min⁻¹ was chosen as it is slow enough to give a fair representation of the crystallisation and melting but fast enough to give reasonable data acquisition times. Ramp rates of 5 and 10 °C min⁻¹ were used when time was more pressing and to give more realistic cooling rates. DSC for the eutectic samples were run at Infineum by Stuart Guy on a TA Instruments Discovery DSC with an auto-sample changer.

2.2.5 Fourier-Transform Infra-Red Spectroscopy

2.2.5.1 Theory

Several different Fourier-transform infra-red spectrometers (FTIR) were used: a Bruker Tensor 27 FTIR spectrometer with an attenuated total reflection (ATR) anvil and a Perkin Elmer Spectrum 100 FTIR with an ATR diamond anvil and a diffuse reflectance (DRIFTS) accessory.

An ATR-IR operates by measuring the changes that occur in an internally reflected IR beam in contact with the sample. An IR beam is directed onto a crystal, typically sapphire or diamond, this creates an evanescent wave that extends beyond the surface of the crystal into the sample, which is held in contact with the crystal. In regions of the IR spectrum where the sample absorbs energy, the wave will be attenuated. This attenuated IR beam is detected as an interferogram signal, which can then be used to generate an IR spectrum. In DRIFTS-IR the beam is focused onto a sample cup filled with powdered sample. The incident beam can be reflected off the surfaces of the particles causing it to scatter. The output mirror then directs this scattered light to the detector generating a spectrum. ATR-FTIR was used to measure the bulk wax and DRIFTS-FTIR was used to measure the surface of the wax.⁷⁸

2.2.5.2 Method

Doped and un-doped model diesel samples were crystallised and the wax filtered from the dodecane using a Grade 1 Whatman filter paper. The filter paper with the wax crystals was left overnight in a fume cupboard to dry. The filtrate was also collected. Reference samples of wax with WASA and dodecane with WASA were made by weighing out the reagents and then melting and re-crystallising the wax or WASA similar to section 2.2.1. The results were analysed using the spectrometer software.

2.2.6 X-ray Powder Diffraction

Doped and un-doped model diesel samples were crystallised, the wax filtered and then left in the fume cupboard to dry. The filtered wax was then lightly ground, in a pestle and mortar, into a fine powder and loaded onto a silicon wafer to put into the Bruker D8 DAVINCI Gen 9 x-ray diffractometer.

2.2.7 X-ray Photoelectron Spectroscopy

A silicon wafer was cut into 1 cm by 1 cm squares. Samples were pipetted onto the silicon and left in a fume cupboard to dry. The samples were sent for measurement to NEXUS at the University of Newcastle. They conducted the X-ray photoelectron spectroscopy depth profile and returned the results which were analysed in the CasaXPS software.

2.2.8 Electrophoresis

2.2.8.1 Theory

Electrophoresis is typically used to determine the charge on a colloidal particle. When two oppositely charged electrodes are placed in a solution containing a charged species, movement occurs as the charged species moves towards its counter electrode due to the applied electrical field. The solution imposes a frictional drag on the species. Thus, the basic net mobility of the species at equilibrium is:

$$\mu = U/E \quad 2.1$$

where μ – electrophoretic mobility, U – velocity and E – electric field. Electrophoresis of colloids is far more complex than for molecules as colloids can display charge, size and shape variation and more complex colloid-colloid interactions.⁷⁹ Ohshima and Kondo proposed a theory for the electrophoresis of large colloidal particles with a surface charge layer. They suggested that electrophoretic mobility decreases as the surface layer thickness increases.⁸⁰

To test whether the WASA generated a surface charge on the wax crystals, two specially designed electrophoresis rigs were used. The design for this rig was based upon the work of Cheekala *et al.* on the removal of soot from diesel systems.⁸¹ Passing 3 kV safely through diesel fuel has been previously reported with electrophoretic mobility results and this was set as the upper voltage limit used in this work.⁸²

2.2.8.2 Methods

The first glass electrophoresis equipment was designed by Andy Price at Infineum. A diagram and photograph are shown in Figure 2.8. A 250 mL Duran round-bottom flat flange reactor with a five-port lid and a PTFE seal was used. Steel wires were fed through two ports, through a PTFE electrode-spacer into the Duran and stainless-steel mesh electrodes were attached *via* PTFE blots. The cables were connected to the electrodes within PTFE stoppers, which were drilled so that the electrical connectors could be held in place whilst sealing the vessel. The vessel was sealed with insulating tape. The electrodes were made from a 4.5 cm by 3.5 cm steel wire mesh, with a 5 mm bent strip on either side to stabilise the electrode. The voltage was supplied by a programmable Consort EV233 power supply.

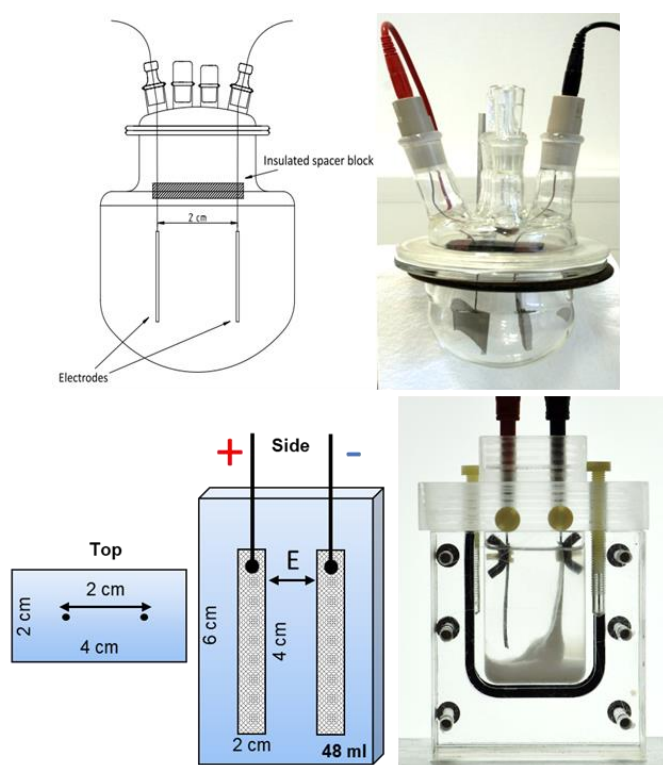


Figure 2.8: Top: Original electrophoresis equipment diagram (left) and photograph (right).
Bottom: Revised Original electrophoresis equipment diagram (left) and photograph (right).

The second electrophoresis equipment was designed by the author and built by Andrew Pluck at the BPI shown in Figure 2.8. It consists of four separate pieces which are bolted together and the electrodes are made from 2 cm by 4 cm steel wire mesh. The electrodes have a 2 cm gap between them. The voltage again was supplied by a programmable Consort EV233 power supply. The rig was filled with roughly 30 ml of sample. For safety reasons the experiment was conducted in a cordoned off fume cupboard. The experiment was filmed via a Canon EOS 1000D camera and a light screen was used to give better contrast photos.

An example voltage procedure, shown in Table 2.7, gives a field strength of 1250 V cm^{-1} at full voltage. The voltage is ramped up slowly for stability of the system to prevent short-circuiting and then held to provide enough time for the wax crystals to migrate.

Table 2.7: Electrophoresis experiment voltage procedure

Ramp to 2500 V over 1 minute
Hold at 2500 V for 5 minutes

2.2.9 Conductivity

The conductance of the WASA in dodecane was measured by a Brookhaven 90Plus/BI-MAS ZetaPlus and an Appleton Woods CM0106 conductivity probe with a Jenway 4020 Conductivity Meter. However, both are not designed for low conductivity non-aqueous systems. Samples of WASA and dodecane were sent to the University of Bristol and tested by Mohamad Danial Shafiq on a more sensitive non-aqueous conductivity meter, using a cylindrical concentric stainless-steel conductivity probe Model 627.

2.2.10 Rheology

2.2.10.1 Theory

Rheology is the study of the flow properties of matter. In a typical experiment, fluid is trapped between a fixed plate and a top plate moving horizontally. The top plate moves at a constant velocity V with force F , as sketched in Figure 2.9. The top plate area in contact with fluid has an area A , the height of the sample is h and δ is the distance moved by the sample.⁸³

The geometry determines the following equations for shear or strain (γ , dimensionless) shear or strain rate ($\dot{\gamma}$, s^{-1}), shear stress (σ , Pa) and shear viscosity (η , Pas):

$$\gamma = \delta/h \quad 2.2$$

$$\dot{\gamma} = V/h \quad 2.3$$

$$\sigma = F/A \quad 2.4$$

$$\eta = \sigma/\dot{\gamma} \quad 2.5$$

Thus, if the applied force and the cross sectional are known a rheometer can be used to measure the viscosity of the sample.⁸³

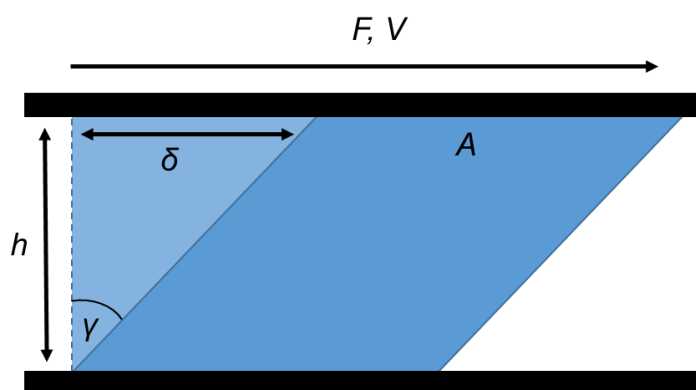


Figure 2.9: Definition diagram for shear flow

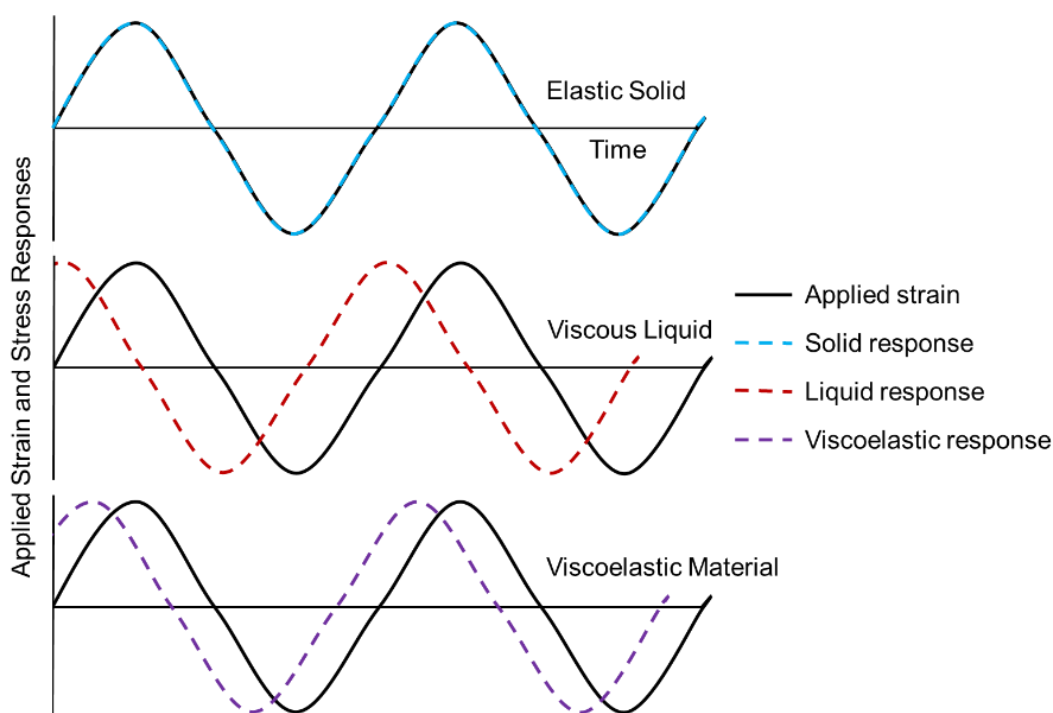


Figure 2.10: Diagram showing response of a solid, liquid and viscoelastic materials to an applied oscillatory strain.

To measure viscoelasticity it is common to apply an oscillatory strain, as shown in Figure 2.10. An elastic material responds in phase to the strain (Figure 2.10 top) whilst a viscous material is shifted by 90° (Figure 2.10 middle). A viscoelastic material behaves intermediately between these two limits (Figure 2.10 bottom).

Viscoelastic samples display both liquid and solid properties when deformed. The solid-like or elastic behaviour is characterised by the storage modulus, G' , and the liquid-like or viscous response is described by the complementary loss modulus, G'' . G^* is called the complex modulus and is a combination of G' and G'' . These can be determined by oscillatory rheology by applying a sinusoidal input stress or strain. The solid-like response will be in phase with the input and the liquid-like response will be $\pi/2$ out of phase with input, see Figure 2.10 and equation 2.7. For an oscillatory applied strain, $\gamma \sim e^{i\omega t}$, in a linear viscoelastic material the shear stress and strain are related by:

$$\sigma = G^* \gamma = (G' + iG'')\gamma \quad 2.6$$

$$\tan \delta = G''/G' \quad 2.7$$

Measurements are normally taken in the linear regime where the modulus and viscosity are independent of applied strain or stress. An amplitude sweep can be used to determine the linear region and then subsequent frequency sweeps *etc.* can be conducted at this stress/strain.

Creep testing can also be used to study viscoelastic materials, see Figure 2.11. The creep compliance, $J(t)$, is a modulus of a creep experiment which consists of applying a shear stress, σ , and monitoring the shear strain, $\epsilon_{xy}(t)$:

$$J(t) = \frac{2\epsilon_{xy}(t)}{\sigma} \quad 2.8$$

Viscoelastic solid materials are commonly modelled by combining springs and dashpots, shown in Figure 2.12. This allows oscillatory and creep testing of viscoelastic materials to be compared using equation 2.9 for creep and 2.10 for oscillatory.

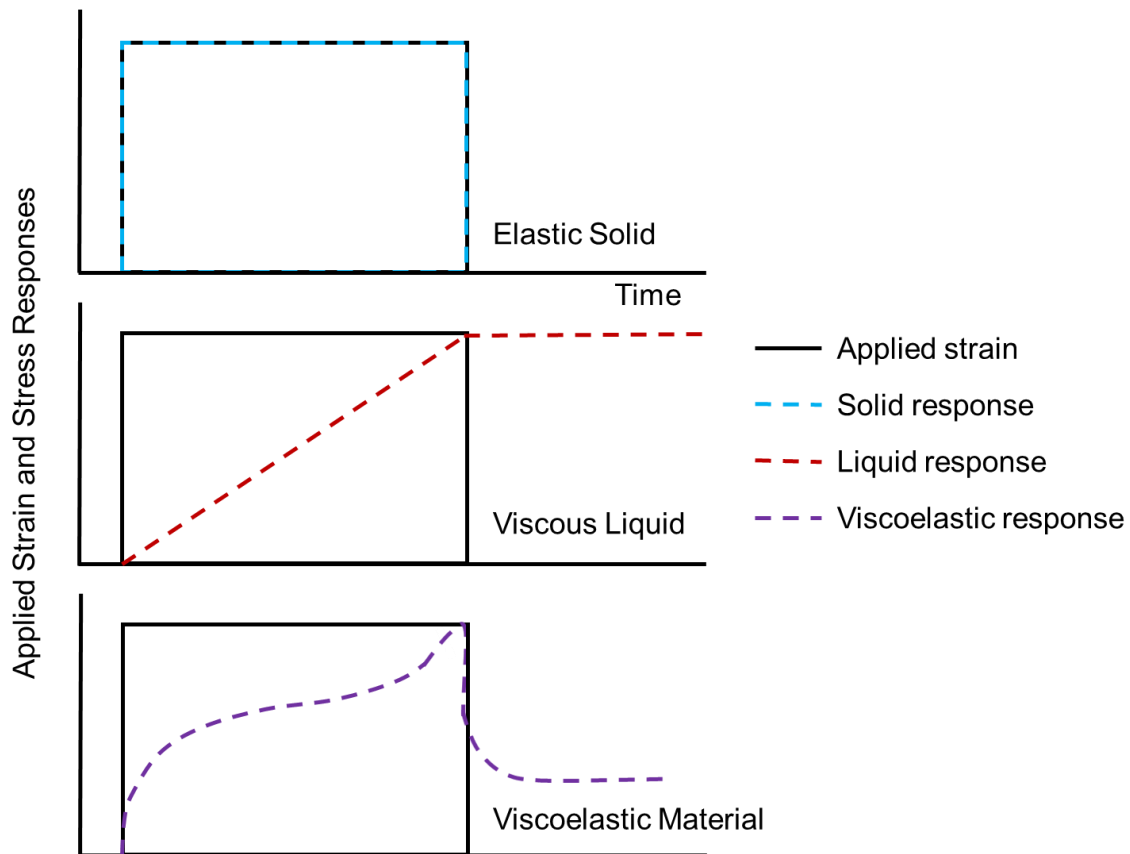


Figure 2.11: Diagram showing response of a solid, liquid and viscoelastic materials to an applied creep strain.

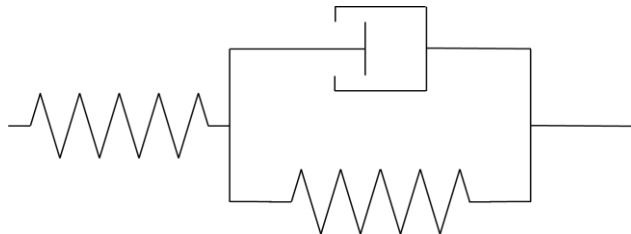


Figure 2.12: Spring and dashpot model of a viscoelastic material

$$J = \frac{1}{G_0} - \left(\frac{1}{G_0} - \frac{1}{G'_\infty} \right) \exp\left(-\frac{G_0 t}{G'_\infty \lambda} \right) \quad 2.9$$

$$\frac{G'}{G'_\infty} = \frac{G_0/G'_\infty + (\lambda\omega)^2}{1 + (\lambda\omega)^2} \quad 2.10$$

Wall slippage has been reported for a wide variety of materials such as particulate glasses⁸⁴ and colloidal gels⁸⁵. Colloidal gels are prone to slipping on the walls of a rheometer due to their macroscopic length scales. Slip can be distinguished by a variable yield stress⁸⁴ and can often be influenced by the interaction, attractive or repulsive, between the colloid and the rheometer.⁸⁶

2.2.10.2 Oscillatory Rheology Method

A Bohlin CS50, Bohlin CVO and Kinexus Lab+ were used for the oscillatory rheology to evaluate the dynamic viscoelastic properties of the samples. All were equipped with a roughened 40 mm parallel plate geometry, to minimise any errors due to slip. Unless otherwise stated the following protocol was used. Samples were heated in an oven to well above their crystallisation temperature (60 – 80 °C). Samples were pipetted hot onto a pre-heated 60 °C bottom plate and the 40 mm roughed top plate was lowered into contact with a gap of 1 mm. Any excess sample was removed with a paper towel. The measurement system was covered to reduce evaporation. A single frequency oscillation test was carried out as the sample was cooled at 2 °C min⁻¹ to 10 °C. The sample was left for at least 5 minutes at 10 °C. Then either a frequency or an amplitude sweep was run at 10 °C to study the gel properties.

2.2.10.3 Creep Rheology Method

Cylindrical pellets of single alkane gels of 20, 40, 60 and 80 wt% of *n*-tetracosane (C₂₄H₅₀) and *n*-octacosane (C₂₈H₅₈) were made using a purpose designed mould (Figure 2.13). The sample containing 10 wt% wax was not used as it was not strong enough to retain its structure during sample loading.

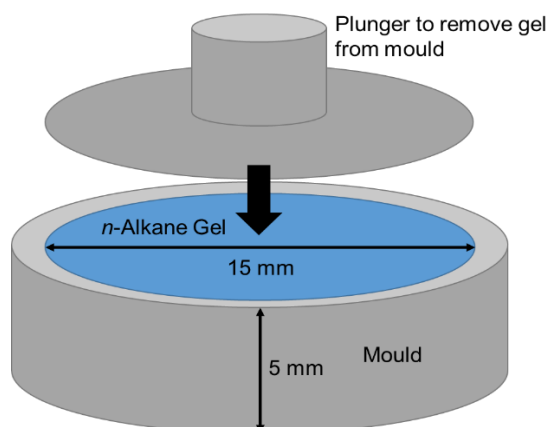


Figure 2.13: Purpose designed mould to make *n*-alkane gel pellets for DMA

A TA Instruments Q800 Dynamic Mechanical Analyser System with compression plates was used to analyse the gels. Both stress and strain-controlled compression tests were conducted.

2.2.10.4 Piezo Axial Vibrator Rheology Method

A Piezo Axial Vibrator (PAV) rheometer was used to detect any increase in viscosity of dodecane upon the addition of WASA. PAV is a dynamic squeeze flow rheometer which operates at frequencies between 1 to 10,000 Hz and is

commonly used on low viscosity polymeric solutions.^{87,88} The PAV consists of a dynamic press with a thin gap in which liquid is confined. A squeeze flow is generated by a piezo electric drive and the response of the system is measured by piezo-sensors (Figure 2.14).



Figure 2.14: Photograph of the PAV cell. The top plate is shown in front of the cell together with one of the stainless steel micro-foil spacing rings.

Samples of WASA in dodecane were ran in the PAV by Dr Simon Butler from the Chemical Engineering and Biotechnology department.

2.2.11 Wax Settling

Previous industry settling tests have been conducted by using a graduated cylinder and give mainly qualitative information. Time lapse photography images of wax settling within the model diesel were taken on a Canon EOS 1000D camera using Digicam software to take a photo every 10 seconds. A light screen was used to give better contrast photos (Figure 2.15).



Figure 2.15: Example set up of wax settling testing

These photos were then analysed by detecting the intensity change of each pixel, using two different MatLab scripts. One written with help from Dr. Peter Dudfield and the other written by Dr. Finn Box of the BPI Fluid Dynamics group.

2.2.12 Small Angle Neutron Scattering

2.2.12.1 Theory

The first small-angle neutron scattering (SANS) instrument was constructed over 40 years ago. It is now a well-established method for micro and nanostructure characterisation. SANS instruments can be either continuous reactor based using monochromated neutron beams, such as the NIST Centre for Neutron Research in Washington DC, or time-of-flight instruments at pulsed spallation neutron sources, such as ISIS in Oxford. Both these sources were used during the course of this PhD. A neutron beamline is made of many components and its exact set up depends on the neutron source, detection required, sample environment, neutron flux and resolution. In its simplest guise a SANS beamline requires a monochromatic, collimated neutron beam, a sample to scatter and a detector, as shown below.⁸⁹

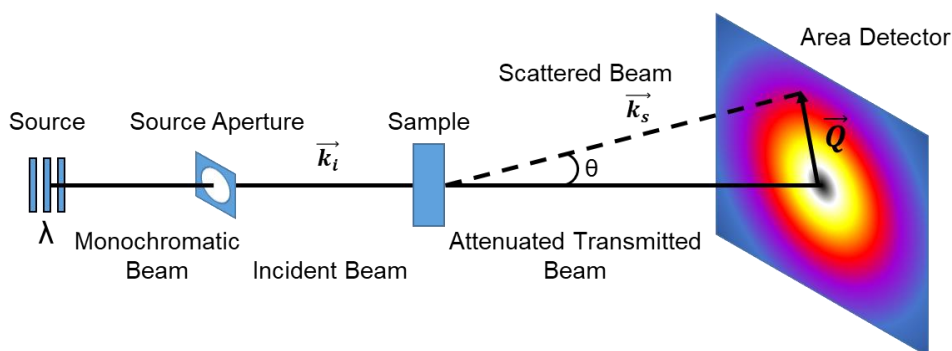


Figure 2.16: Schematic of a SANS experiment.

Neutrons are both a bulk and surface probe. They interact through short-range nuclear interactions and are very penetrating but do not damage or perturb the sample. Neutron wavelengths are comparable to atomic sizes. They also have very different interactions, and thus scattering length densities, between hydrogen and deuterium giving the advantage of contrast over x-ray scattering.

In small angle diffraction a pattern is obtained in reciprocal space using a scattering vector Q (nm^{-1} or $\text{\AA}^{-1}$). Q is the difference between the incident and scattered wave. λ is the neutron wavelength and θ is the scattering angle.⁹⁰

$$Q = k = \frac{4\pi}{\lambda} \sin(\theta/2) \quad 2.11$$

$$Q \approx 2\pi/d$$

Small Q probes large distances while large Q probes small distances.

The neutron beam is typically 8 – 12 mm in diameter. The intensity $I(Q)$ of the scattered neutron beam, called the absolute scattering cross section ($\partial \Sigma Q / \partial \omega$, cm^{-1}), is the probability of a neutron wavelength, λ , being scattered per unit solid angle at that Q . Scattered neutrons detected in an area, A , and efficiency, η , at radius, R , and distance, L , from the sample with a solid angle ($\Delta\Omega = A/L^2$), sample thickness, t and sample transmission, T are:

$$I(Q) = I_o(\lambda) \frac{\delta \Sigma Q}{\delta \Omega} \Delta\Omega(R) t T(\lambda) \eta(\lambda) \quad 2.12$$

where $I(Q)$ contains all the information of size, shape and interactions between the scattering samples in the sample. For monodisperse homogenous spheres $I(Q)$ can be defined as:

$$I(Q) = NV^2 \Delta\rho^2 P(Q) S(Q) + B \quad 2.13$$

where N – number of scattering spheres, V – volume of a sphere, $\Delta\rho$ – different in scattering length densities. $P(Q)$ is the form factor which gives intra-sphere information such as size and shape. The larger the scattering object the more steeply $P(Q)$ falls off with Q . $S(Q)$ is the structure factor which gives inter-sphere information such as if they are repulsive or attractive. $S(Q)$ is equal to 1 for dilute non-interacting systems.

The scattering length density, SLD , of a molecule is calculated by its density, ρ , molecular mass, M , Avogadro's constant, N_a , and the average atomic scattering length, b :

$$SLD = N \sum b = 10^{-24} \frac{\rho}{M} N_a \sum b \quad 2.14$$

Hydrogen and deuterium have very different SLD 's allowing us to use deuterated materials to provide contrast and contrast matching, as shown in Figure 2.17. This means that SANS is a powerful tool to probe individual aspects of a sample *in situ*.

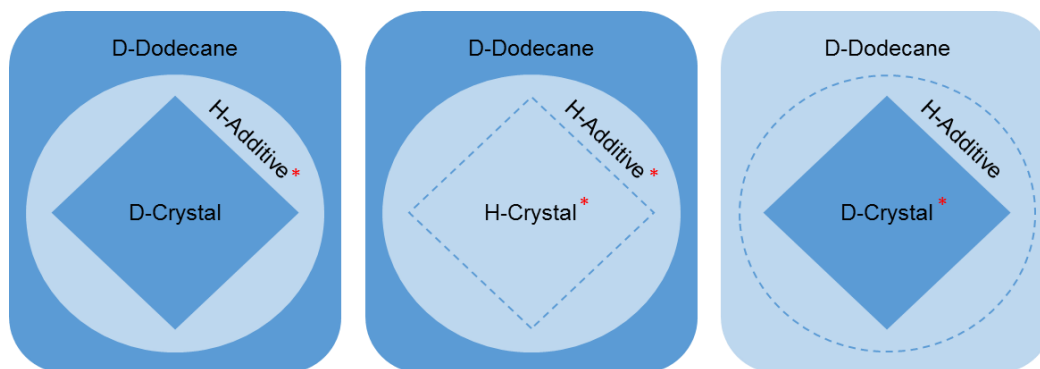


Figure 2.17: Diagrams showing how use of deuterated sample elements can highlight, indicated by *, different aspects of the sample.

From left to right; the D-crystal is contrast matched out by the D-Dodecane and the H-additive is highlighted; the H-Additive and H-Crystal are highlighted but contrast matched by each other due to D-Dodecane; the D-Crystal is highlighted while the H-Additive is contrast matched out by the H-Dodecane.

Once the scattering data is obtained the data is reduced according to that beamlines' procedure, using Mantid software for ISIS and Igor software for NIST. This removes any instrument specificity so data sets can be compared. Numerous software packages are available to analyse and fit the data. SASView was used in this work. Standard plots, such as the Guinier or Porod plots, can be used to yield analysis after reduction. The Porod plot of $\text{Log}(I(Q))$ vs. $\text{Log}(Q)$ yields information about the fractal dimension of the scattered objects:

$$I(Q) = AQ^{-n} \text{ or } \log I(Q) = \log A - n \log Q \quad 2.15$$

The slope of the Porod plot or n the Porod exponent can give indications as to the structure of the scattered sample and its surface or mass fractal. For example, a large 3D object with a rough surface will have a Porod exponent of $3 < n < 4$. More Porod exponent examples can be seen in Figure 2.18.

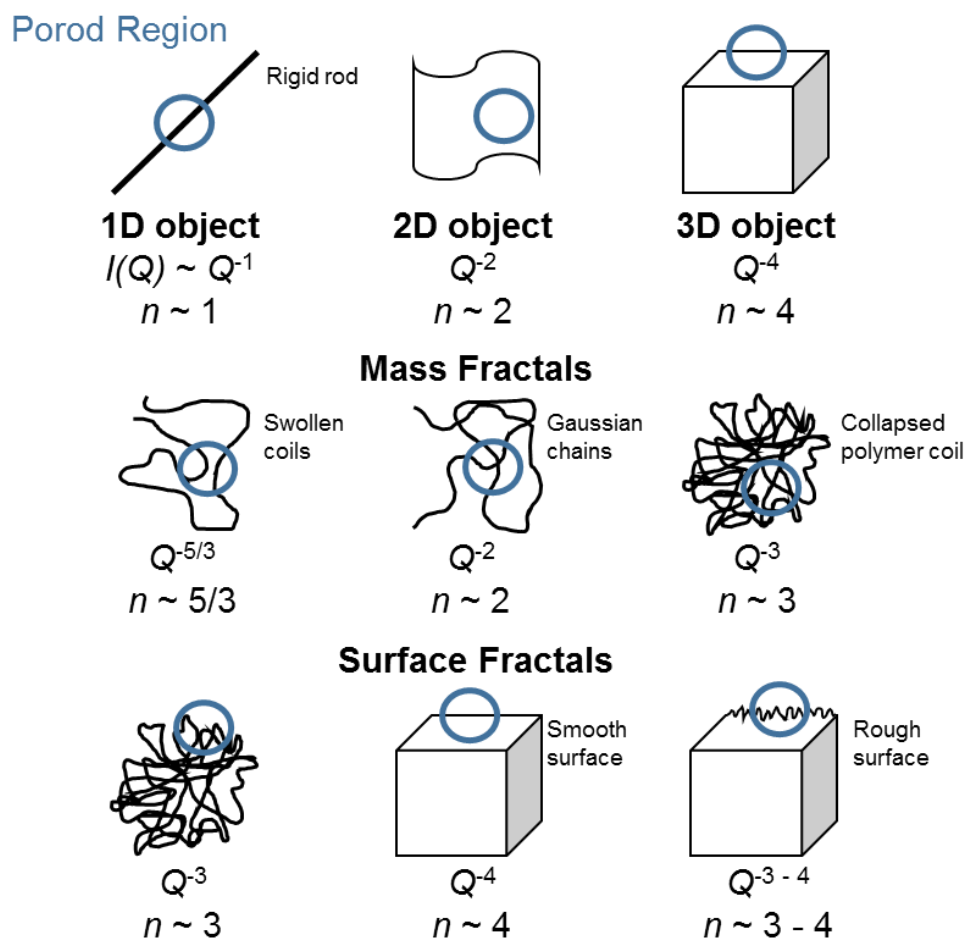


Figure 2.18: Examples of Porod exponents

2.2.12.2 Method

SANS was conducted at the NIST Centre for Neutron Research in Washington and ISIS in Oxford. At NIST beamlines USANS BT5 and NG7 were used and at ISIS the SANS2D beamline was used.

Table 2.8: Configuration and resulting Q-range of neutron beamlines used

Beamline	Q-range ($\text{\AA}^{-1}$)
BT5	2.7E-06 – 2.7E-03
NG7	3.3E-03 – 1.2E-01
SANS2D	1.6E-03 – 4.9E-01

Doped and un-doped model diesel samples were prepared using purchased and synthesised deuterated materials. They were melted and stored in a 60 °C oven and then pipetted into quartz banjo cells; 1 mm thick for hydrogen solvents and 2 mm thick for deuterium solvents. The banjo cells were placed in the temperature-controlled sample holder prior to them being run to allow for equilibration time.

Samples were run at 15, 20, 25, 30 and 40 °C with 10 wt% wax model diesel and differing concentrations of additives.

The *SLD* of the materials used in the samples are listed below;

Table 2.9: Scattering Length Densities of materials used in SANS samples.

Component	H-contrast ($\text{\AA}^{-2}$)	D-contrast ($\text{\AA}^{-2}$)
H-WASA	-1.20E-07	
Dp-WASA	-	8.98E-08
D-WASA	-	1.12E-06
Dodecane	-4.63E-07	6.43E-06
Wax*	-3.86E-07	6.11E-06
* Wax SLD is averaged over C_{20} , C_{24} , C_{28} and C_{32} alkanes.		

The contrasts used are shown below in Figure 2.19. All elements in the model diesel can be purchased deuterated and the additives can be synthesised using deuterated components. So the samples could be made progressively more complex:

1. Just the wax only in dodecane in the two contrasts; D-wax in H-dodecane and H-wax in D-dodecane.
2. The additives in dodecane in two contrasts; D-additives in H-dodecane and H-additives in D-dodecane.
3. The full model formulation with additives and wax in dodecane in six contrasts; H-additive, D-wax in D-dodecane highlighting the additive, H-additive, H-wax in D-dodecane highlighting the additive and wax together and H-additive, D-wax and H-dodecane highlighting the wax and the next three contrasts with the opposite isotopic selection.

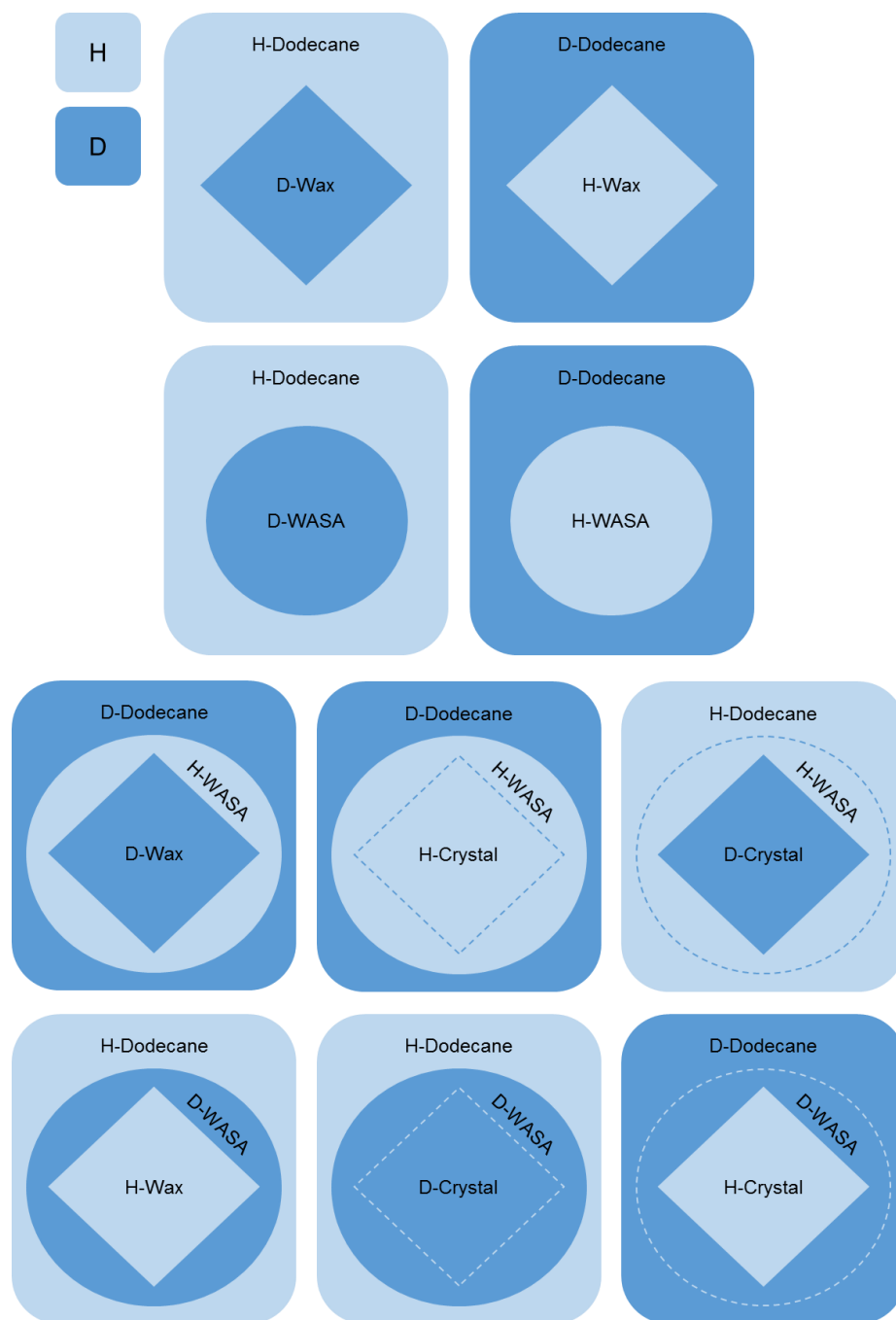


Figure 2.19: Diagram showing the contrasts used on SANS. From the top; wax in dodecane in two contrasts, additives (WASA or FVA) in dodecane in two contrasts and additives (WASA or FVA) with wax in dodecane in six contrasts.

2.2.13 Turbidity and Solubility

Samples of additives in dodecane were made by weighing out the reagents and then melting and re-crystallising the additives. Turbidity measurements were performed over a temperature range of -15 to 60 °C on an Avantium Technologies Crystal 16 based at Infineum. The Crystal 16 is used to measure the solubility of the additives as it measures the turbidity of the sample as it is cooled, when the transmittance drops below 100% additives have precipitated out of solution.

The solubility of the additives was also measured by placing the samples in a water bath on a hot plate and in a sonicator. The temperature of both was increased by 1 °C every 2 minutes from room temperature to the temperature at which all the samples were dissolved.

2.2.14 Dynamic Light Scattering

2.2.14.1 Theory

Laser light is shone through a colloidal suspension. The Brownian motion of particles or molecules causes the scattered light intensity to fluctuate (Figure 2.20). Analysis of these intensity fluctuations yields the rate of the Brownian motion and hence the particle size using the Stokes-Einstein relationship.

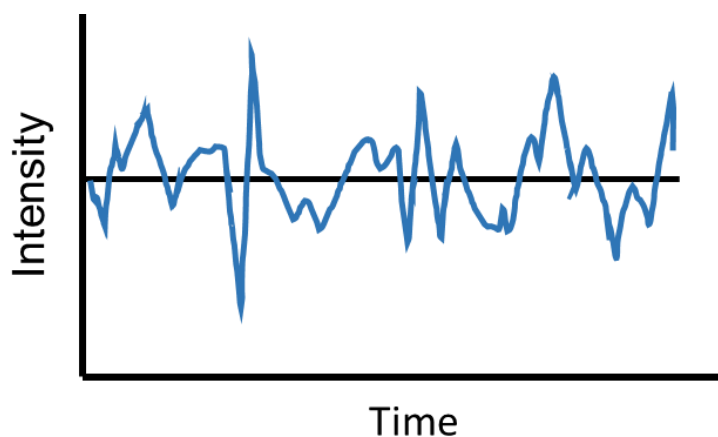


Figure 2.20: Laser fluctuations about the average scattered intensity.

2.2.14.2 Method

Sizes were obtained on a Brookhaven 90Plus/BI-MAS ZetaPlus dynamic light scatter (DLS) with ZetaPlus Particle Sizing Software (MAS OPTION). Samples of wax or additives in dodecane were made by weighing out the reagents and then melting and re-crystallising the wax or additives. The sample was transferred to a glass cuvette. If the DLS showed the sample to be too dusty for a good measurement the sample was remade with filtered dodecane (using 0.2 µm PTFE filters). The temperature of the DLS can be varied allowing the crystallisation of the sample to be viewed.

2.2.15 Interfacial tension measurements

Interfacial tension measurements were made using the pendant drop method on a Kruss DSA 100. De-ionised water from an Elga Purelab ultra was washed through a syringe and 1.83 mm diameter needle until the air-water interfacial tension measured using the Young-Laplace fit was consistently $72 \pm 2 \text{ mN m}^{-1}$.

Once it was established that the needle was sufficiently clean the dodecane-water interfacial tension was measured. This was achieved by submerging the needle in a square glass bath of dodecane and measuring the resulting water drop profiles. The dodecane used was un-purified and anhydrous thus the dodecane-water interfacial tension literature value of 52.7 mN m^{-1} was not expected to be achieved. The bath was washed with dodecane until the dodecane-water interfacial tension was stable at $48 \pm 1 \text{ mN m}^{-1}$ for 2 minutes. Increasing wt% amounts of WASA was dissolved in dodecane in a 60°C oven and then left to cool overnight. This doped dodecane was put in the cleaned glass bath and the interfacial tension measured.

3 Results – Model Diesel and Location of WASA

3.1 Designing model diesel

Previous work (at Infineum) was conducted on a petroleum diesel with a wax appearance temperature of -2 °C. Experiments were typically conducted between -18 °C and -25 °C. This severely limits the experiments that can be conducted, due to issues with condensation and sensitive equipment not working at sub-zero temperatures. Thus, it was advantageous to develop a model diesel which crystallises at room temperature. This model needed to show similar responses to additives and WASAs as petroleum diesel; this required balancing the total weight percent of waxy *n*-alkanes and amount of additive. Model diesel mixtures were prepared according to the method described in section 2.2.1 and additives were added according to section 2.2.2.

The effect of additives on the model can be visually inspected. If the model still gels with large wax crystals upon addition of the additives, this indicates that the additives are having a limited effect. If no crystals form in the system, this indicates that the additives are having a large effect and are shifting the crystallisation temperature to below room temperature. Ideally, a cloudy solution would be observed at room temperature with small crystals in suspension or a gel, meaning that the additives are affecting the crystallisation of the wax, mimicking the behaviour of petroleum diesel.

3.1.1 Mixed vs single waxy alkanes

3.1.1.1 Single waxy alkanes

The solvent used was dodecane, however this only models the aliphatic components of diesel not the aromatic components, whereas an 80:20 mix of heptane:toluene is commonly used in industry. This was done to simplify the model.

A wax percentage of 30 wt% was initially used as this is the amount commonly present in petroleum diesel. 30 wt% mixtures of single waxes with chain lengths C₂₀, C₂₄, C₂₈ and C₃₂ were tested, each with and without 0.1 and 0.5 wt% WASA.

However, each system fully gelled with large wax crystal plates forming an interlocking network across the system, consequently the wax loading was reduced to 10 wt%.

10 wt% mixtures of single waxy alkanes with chain lengths of C_{20} , C_{24} , C_{28} and C_{32} were tested, each with and without 0.1 and 0.5 wt% WASA. C_{20} did not crystallise out of solution at room temperature and all other waxy alkanes gelled upon crystallisation as seen in Figure 3.1. This initial experiment showed that only waxes C_{24} and above have high enough crystallisation temperatures. However, the WASA additive on its own doesn't seem to have a large impact on the crystallisation to prevent the gel forming.



Figure 3.1: 10 wt% mixtures of single waxy alkanes; C_{20} , C_{24} , C_{28} and C_{32} , with and without 0.1 and 0.5 wt% WASA at roughly 18 °C. From left to right; C_{20} , $C_{20}+0.1$ wt% WASA, $C_{20}+0.5$ wt% WASA; C_{24} , $C_{24}+0.1$ wt% WASA, $C_{24}+0.5$ wt% WASA; C_{28} , $C_{28}+0.1$ wt% WASA, $C_{28}+0.5$ wt% WASA; C_{32} , $C_{32}+0.1$ wt% WASA, $C_{32}+0.5$ wt% WASA.

5 wt% mixtures of the single waxy alkanes C_{24} and C_{28} with 0.1 and 0.5 wt% WASA were tested. C_{24} did not crystallise out of solution at room temperature (roughly 18 °C) and C_{28} crystallised and gelled. This suggests 5 wt% is too little wax for the shorter chain lengths to crystallise at room temperature thus 10 wt% wax was used. Compared to petroleum diesel 10 wt%, of these longer chain alkanes is high, as the *n*-alkane wax distribution of diesel is very broad and much of the weight percent is made up of smaller chain *n*-alkanes which do not cause the cold flow problems. To counteract this, a higher concentration of additives than normal industrial levels could be used.

Industrial knowledge has suggested that WASA is more effective when used in conjunction with other additives. Because of this, a mixture of 0.1 wt% WASA and 0.1 wt% C_{22} FVA were doped into the 10 wt% single wax mixtures however, these also gelled.

The additives appear to have an inability to affect the crystallisation of single waxes enough to prevent the growth of the large plate wax crystals and the formation of a gel. Thus 10 wt% *n*-alkane mixtures were tried.

3.1.1.2 Mixture of waxy alkanes

A 10 wt% mixture of equal amounts of C₂₀, C₂₄ and C₂₈ were tested, with various combinations of C₂₂ FVA and WASA totalling 0.2 wt% additive concentration. At room temperature most of the samples appeared clear. This was surprising, as the single waxes gelled at this temperature, and the wax mixture without any additive weakly gelled. When the mixtures were placed in a 5 °C fridge the wax crystallised into small slurry-like crystals which settled. The results are shown in Table 3.1 and Figure 3.2.

*Table 3.1: 10 wt% C₂₀, C₂₄ and C₂₈ mixture multiple *n*-alkanes mixtures doped with FVA and WASA*

#	WASA (wt%)	C ₂₂ FVA (wt%)	25 °C	5 °C
22	0.04	0.16	Clear	Small crystals, slurry like
23	0.1	0.1	Clear	Small mostly settled crystals
24	0.016	0.04	Clear	Small mostly settled crystals



*Figure 3.2: 10 wt% multiple *n*-alkanes mixtures observation results # 22 to 24. Left at 25 °C and Right at 5 °C.*

This shows that the additives are having a far greater effect on the wax mixture than they did on the single wax samples. However, because an ideal target system would crystallise at room temperature, the crystallisation temperature needed to be raised. Consequently, a longer chain 10 wt% mixture of C₂₄, C₂₈ and C₃₂ was tested with the same additive doping. These mixtures formed a more successful room temperature diesel model. The waxes crystallised at room temperature and the crystals formed were reduced in size and did not gel the system.

Following this, a 10 wt% mixture of equal amounts of C₂₀, C₂₄, C₂₈ and C₃₂ was tested. This gives a broader range of wax chain lengths to the model diesel, more

closely mimicking petroleum diesel. This mixture crystallised at room temperature and had a similar response to additives as petroleum diesel as seen in Figure 3.3 compared to Figure 1.1. Due to the high degree of similarity between this system and that of petroleum diesel, this was model diesel mixture that was used throughout the rest of this work.

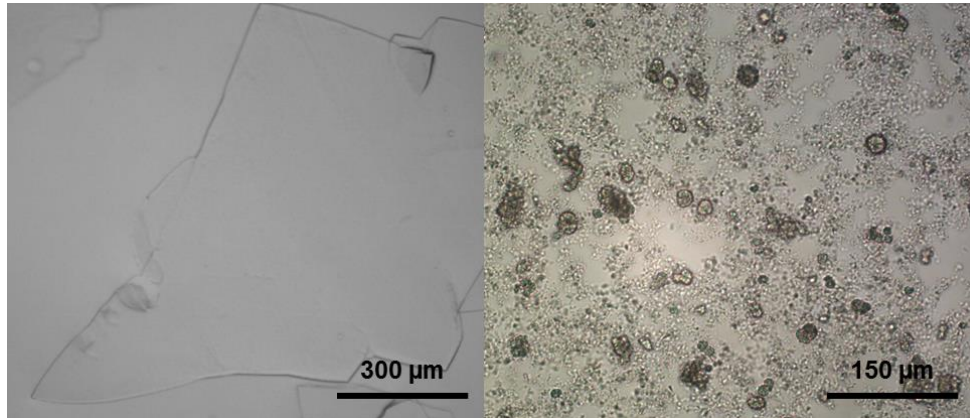


Figure 3.3: Left – Wax crystal from model diesel without any additives. Right – Wax crystal from model diesel with WASA

3.2 Effect of additives on model diesel

Once a model diesel system had been developed, further understanding of the effect of the additives on the shape, size and crystallisation temperature of the wax crystals was required.

3.2.1 Phase diagram

To try and further understand the parameters of this model diesel, a phase diagram at room temperature was created to ascertain the effect of varying the additive wt% on the 10 wt% *n*-alkane mixture model diesel. Table 3.2 shows additive doping into the model diesel.

Table 3.2: Amounts of EVA, FVA and WASA doped into the 10 wt% model diesel

#		Additive (wt%)		#		Additive (wt%)	
0	No additives	-	-	15	EVA + WASA (1:4)	0.1	0.4
1	WASA	0.05	-	16	C_{22} FVA + WASA (1:4)	0.2	0.8
2		0.1	-	17		0.01	0.04
3		0.5	-	18		0.02	0.08
4		1	-	19		0.1	0.4
5	EVA	0.05	-	20	C_{22} FVA + WASA (4:1)	0.2	0.8
6		0.1	-	21		0.04	0.01
7		0.5	-	22		0.08	0.02
8		1	-	23		0.4	0.1
9	C_{22} FVA	0.05	-	24	C_{22} FVA + WASA (1:1)	0.8	0.2
10		0.1	-	25		0.025	0.025
11		0.5	-	26		0.05	0.05
12		1	-	27		0.25	0.25
13	EVA + WASA (1:4)	0.01	0.04	28		0.5	0.5
14		0.02	0.08				

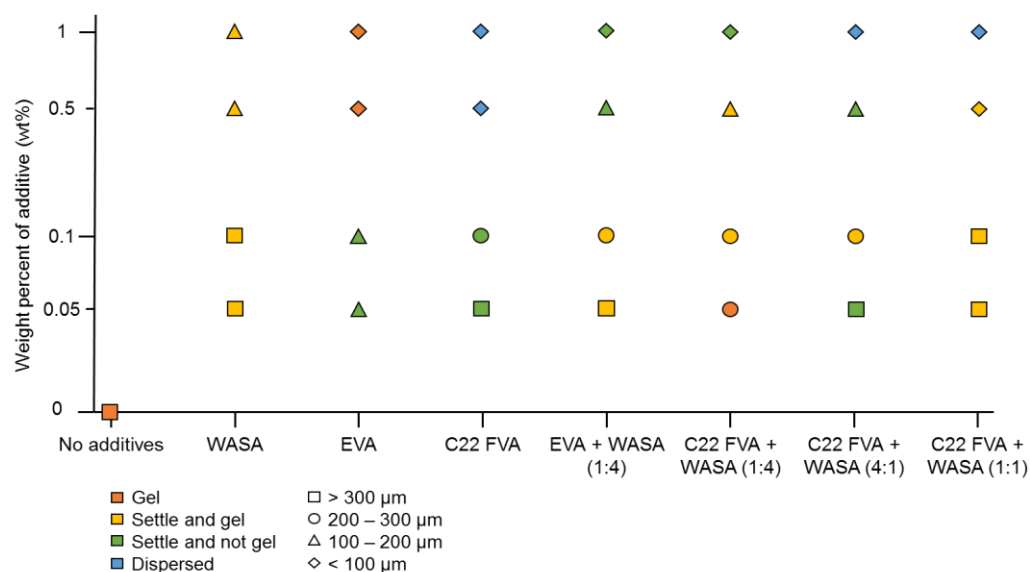


Figure 3.4: Phase diagram of additive doped into 10 wt% model diesel showing crystal size and effect on system

A phase diagram showing the results of the additive doping on the model diesel is shown in Figure 3.4. Observations were taken after the sample was left to crystallise overnight and then left at room temperature for a day. As expected, without any additive present the model diesel gels at room temperature. Generally, increasing the amount of additive decreases the occurrence of gelling and the crystal size. In the presence of WASA, the crystals settle and gel. In the presence of EVA at lower wt% the crystals settle but don't gel, whilst at higher wt% the system gels. In the presence of C₂₂ FVA, at lower wt% the crystals settle but don't gel, whilst at higher wt% the crystals remain dispersed.

With the 1:4 EVA and WASA additive mixture the wax crystals with lower doping settled and gelled and at higher doping settled and did not gel. The 1:4 C₂₂ FVA and WASA gelled at 0.05 wt%, settled and gelled and then settled and didn't gel as wt% increased. The 4:1 C₂₂ FVA and WASA settled and did not gel at 0.05 and 0.5 wt%, settled and gelled at 0.1 wt% and remained dispersed at 1 wt%. The 1:1 C₂₂ FVA and WASA settled and gelled at lower wt% and remained dispersed at 1 wt%.

The phase diagram shows that the presence of the WASA alone does not prevent the model system from settling over a day, but that the settled crystals are more likely to gel, even when used in combination with other additives. C₂₂ FVA is the most effective additive in decreasing the crystal size and thus dispersing the wax crystals – both of which are desirable behaviours.

Interestingly, the model diesel also gels at high ppm amounts of EVA even though the crystal size is small at $\sim 20\ \mu\text{m}$ (Figure 3.5). This could be due to a larger volume of smaller wax crystals being nucleated by the EVA and gelling the system due to their number. Alternatively, it could be due to the polymeric EVA having a depletion effect on the system.

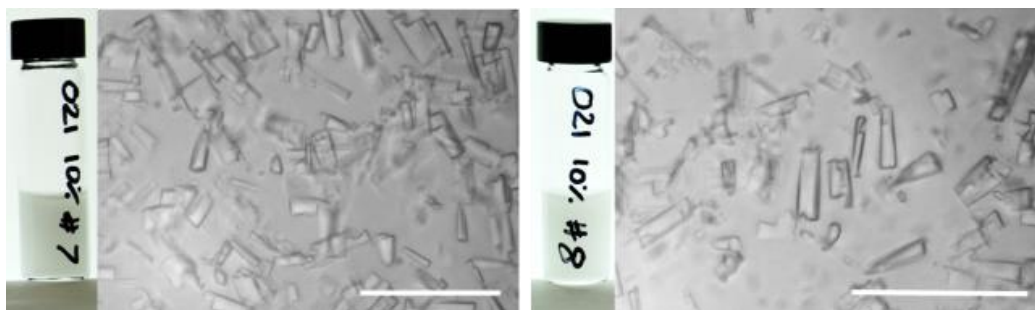


Figure 3.5: Photographs showing gelation of #7 and 8 and optical microscope images of the wax crystals with the white line indicating $50\ \mu\text{m}$.

3.2.1.1 Optical Microscopy images

Optical microscopy shows that the size of the crystals decreases with increasing amounts of additive doping as shown in Figure 3.6. Without any additives the wax crystals form as large rhombic wax crystal plates with a longest length of over $300\ \mu\text{m}$. Increasing the WASA doping decreases the crystal size and changes the crystals' morphology to more cuboid, nugget-like crystals. Increasing the EVA doping decreases the crystal size to below $50\ \mu\text{m}$ and changes the crystal morphology to a needle-like shape. This is true even at low concentrations, which agrees with EVA acting as a nucleator. Increasing the C_{22} FVA doping decreases the crystal size to below $10\ \mu\text{m}$ and, like the WASA, changes the crystals morphology to more cuboid, nugget-like crystals. EVA and C_{22} FVA are the most effective at decreasing the wax crystal size whereas for the WASA to affect the wax crystal size higher wt% concentrations must be used.

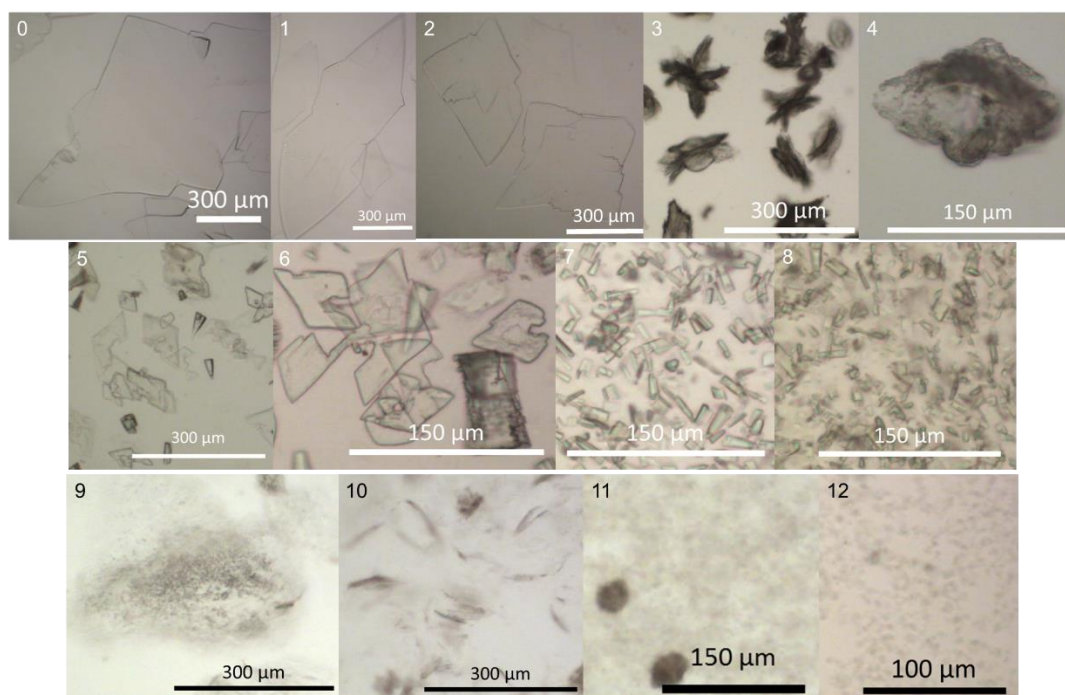


Figure 3.6: Optical microscopy images showing samples 0 – 12 as defined in Table 3.2 (left to right, top to bottom).

In order to measure how effective the WASA is at reducing wax crystal size, the longest length (*i.e.* largest crystal dimension) of 100 wax crystals from the WASA doped model diesel were measured via optical microscopy. The distribution of the longest lengths is shown in Figure 3.7. As the doping of WASA increases, the mean longest length and the standard deviation decreases as shown in Table 3.3.

Table 3.3: The mean longest length and standard deviation of wax crystals doped with increasing amounts of WASA.

WASA (wt%)	Mean longest length (μm)	Standard Deviation (μm)
0	285	149
0.01	219	113
0.05	167	57
0.1	128	53
0.5	38	13
1	16	12

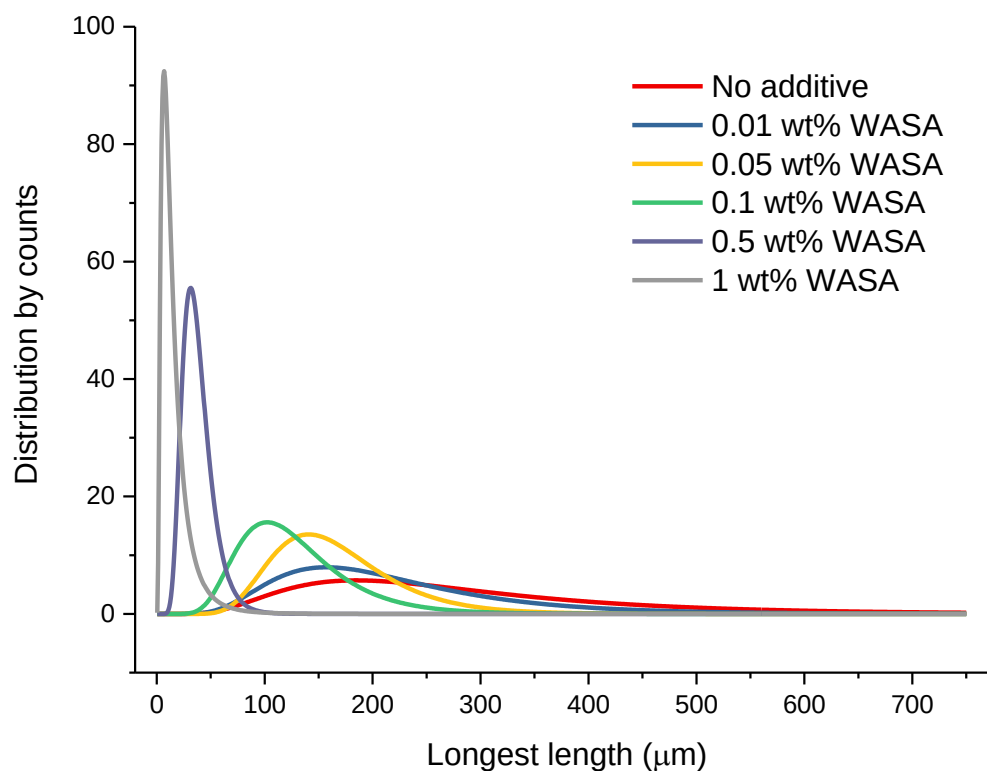


Figure 3.7: Distribution of longest length of 100 wax crystals from model diesel and WASA doped model diesel.

3.2.1.2 Differential scanning calorimetry

The crystallisation temperature, T_c , of the samples listed in Table 3.2 was measured by differential scanning calorimetry (DSC). The graph in Figure 3.8 shows the difference in T_c between the model diesel with and without any additives: $\Delta T_c = T_c(\text{doped model diesel}) - T_c(\text{model diesel})$. Larger differences correspond to the additives more dramatically decreasing the T_c .

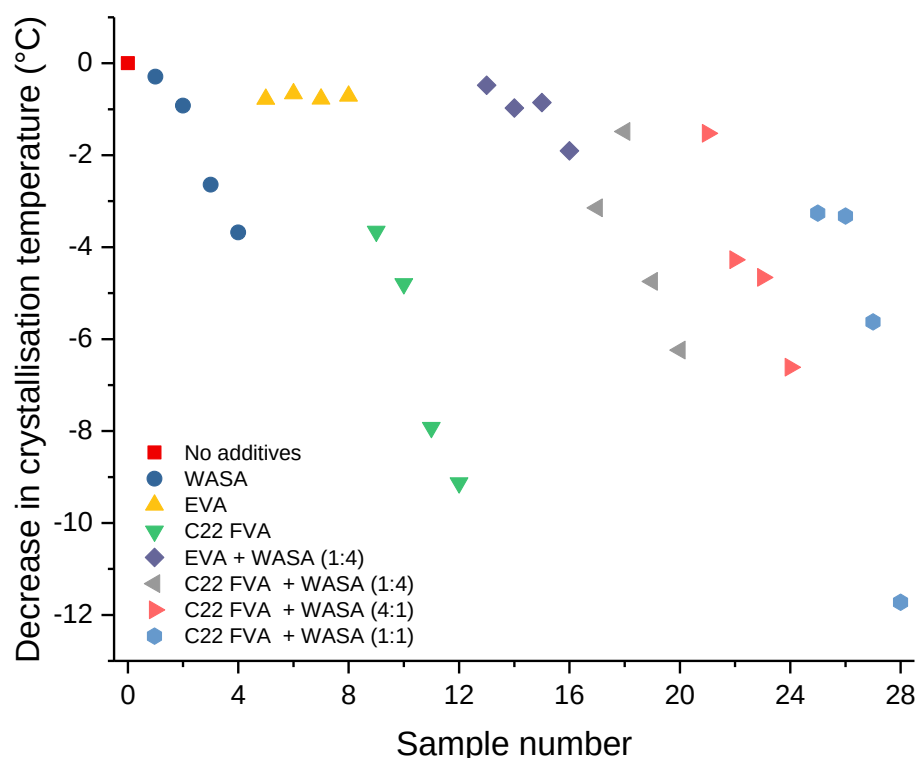


Figure 3.8: Graph showing the difference in crystallisation temperature between the model diesel with and without additives.

For all combinations of additives tested, the T_c of the model diesel is decreased from the case with no additives. The T_c of the model diesel was 20 °C. This means that the additives successfully suppressed the crystallisation temperature. Increasing the doped amount of WASA decreased T_c of the wax. EVA did not have a great effect and increasing the amount of EVA did not change this. This is again consistent with EVA acting as a nucleator. C₂₂ FVA has the largest effect on the T_c showing a drop of 9 °C at 1 wt% doping. 1:4 EVA and WASA do not decrease T_c dramatically, again due to EVA being a nucleator. 1:4 and 4:1 C₂₂ FVA and WASA decrease the T_c a similar amount, while 1:1 C₂₂ FVA and WASA decreases the T_c significantly.

DSC also shows small amounts of WASA suppressing T_c . Moreover, the shape of the DSC curve also changes as shown in Figure 3.9. This indicates that the WASA is incorporated into the wax crystal.

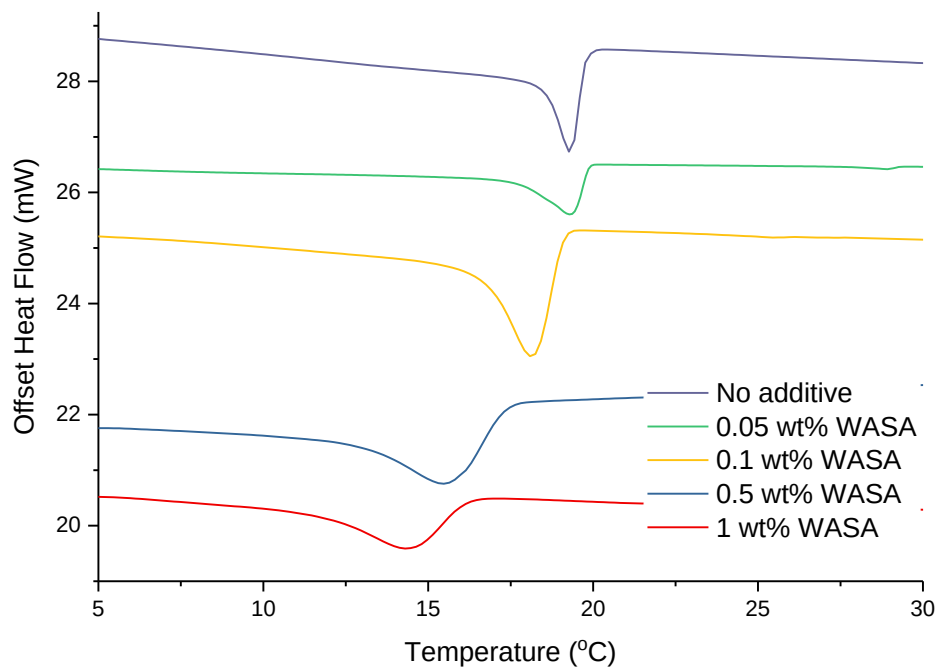


Figure 3.9: Differential scanning calorimetry cooling trace of model diesel with increasing wt% amounts of WASA

If the amount of WASA doped into the model diesel is increased, the decrease in T_c plateaus as seen in Figure 3.10. After 2.5 wt%, there is no additional benefit of adding more WASA, in terms of decreasing T_c .

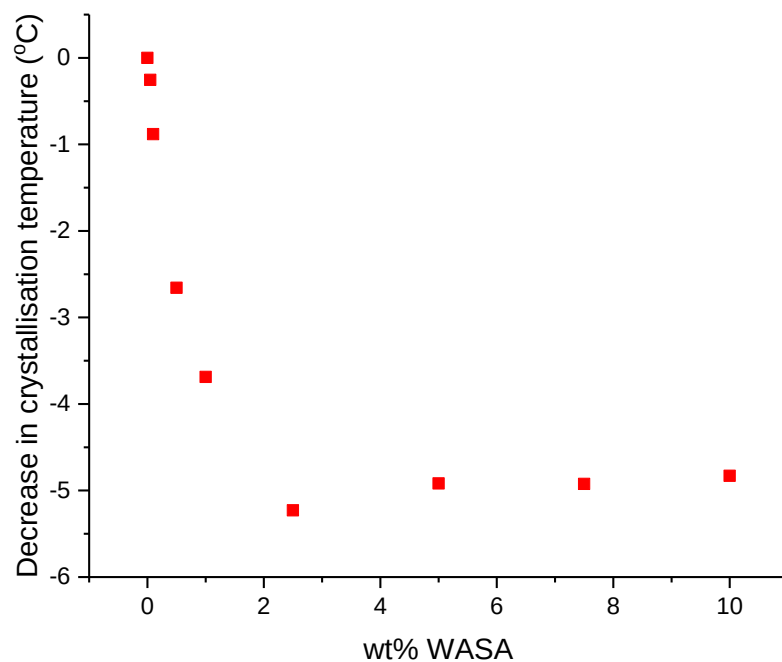


Figure 3.10: Decrease in crystallisation temperature of model diesel upon addition of 0.05 to 10 wt% WASA

3.2.2 WASA and C₂₂ FVA chain matching

Additives are thought to co-crystallise with the wax crystals, thus the chain lengths of the aliphatic components of the additives should match those of the waxes. *n*-Alkanes of chain lengths C₁₂ to C₃₂ were doped with WASA or C₂₂ FVA to determine the decrease in crystallisation temperature (T_c) upon addition of the additive. A larger decrease indicates that the additive is more effective. Figure 3.11 shows the difference in T_c between pure 10 wt% single *n*-alkane waxes in dodecane and the same chain length doped with 0.1 wt% of WASA or C₂₂ FVA.

Of the single *n*-alkanes, WASA had the largest decrease in T_c on C₁₆. This could be due to chain matching of the C_{16/18} tail of the WASA with the *n*-alkane which is closest in length. Similarly, the largest decrease in T_c with C₂₂ FVA is the C₂₄ chain length *n*-alkane. Again, this could be due to chain matching.

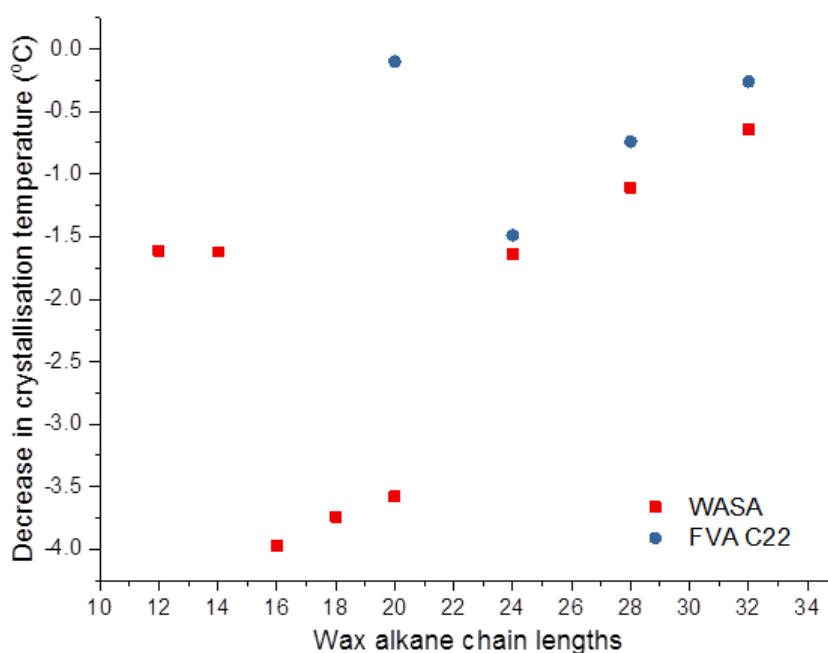


Figure 3.11: Decrease in crystallisation temperature of different *n*-alkane chain lengths upon addition of WASA and FVA C₂₂

3.2.3 Co-crystallisation and eutectic measurements

Eutectic measurements using differential scanning calorimetry (DSC) were conducted to help determine the extent to which the decrease in crystallisation temperature, T_c , upon addition of WASA is due to the WASA action or is simply a melting point depression due to mixing.

The eutectic mixing behaviour of the model diesel system was studied using C₂₀, C₂₄, C₂₈ and C₃₂ wax alkanes in combinations with the shorter *n*-alkane added to

the longer at 20, 40, 60, and 80 mole percent (m%) and the same combinations with 10 m% WASA, a sample list is shown in Table 3.4. The samples without 10 m% WASA are shown in black and those with 10 m% WASA are shown in red in Figures 3.12 and 3.13.

Table 3.4: Samples for eutectic DSC testing with different m%

	C₂₀/C₂₄ m%	C₂₀/C₂₈ m%	C₂₀/C₃₂ m%	C₂₄/C₂₈ m%	C₂₄/C₃₂ m%	C₂₈/C₃₂ m%
<i>n</i>-alkanes only	0/100	0/100	0/100	-	-	-
	20/80	20/80	20/80	20/80	20/80	20/80
	40/60	40/60	40/60	40/60	40/60	40/60
	60/40	60/40	60/40	60/40	60/40	60/40
	80/20	80/20	80/20	80/20	80/20	80/20
	100/0	-	-	-	-	-
	C₂₀/C₂₄/WASA m%	C₂₀/C₂₈/WASA m%	C₂₀/C₃₂/WASA m%	C₂₄/C₂₈/WASA m%	C₂₄/C₃₂/WASA m%	C₂₈/C₃₂/WASA m%
<i>n</i>-alkanes and 10 m% WASA	0/90/10	0/90/10	0/90/10	-	-	-
	18/72/10	18/72/10	18/72/10	18/72/10	18/72/10	18/72/10
	36/54/10	36/54/10	36/54/10	36/54/10	36/54/10	36/54/10
	54/36/10	54/36/10	54/36/10	54/36/10	54/36/10	54/36/10
	72/18/10	72/18/10	72/18/10	72/18/10	72/18/10	72/18/10
	90/0/10	-	-	-	-	-

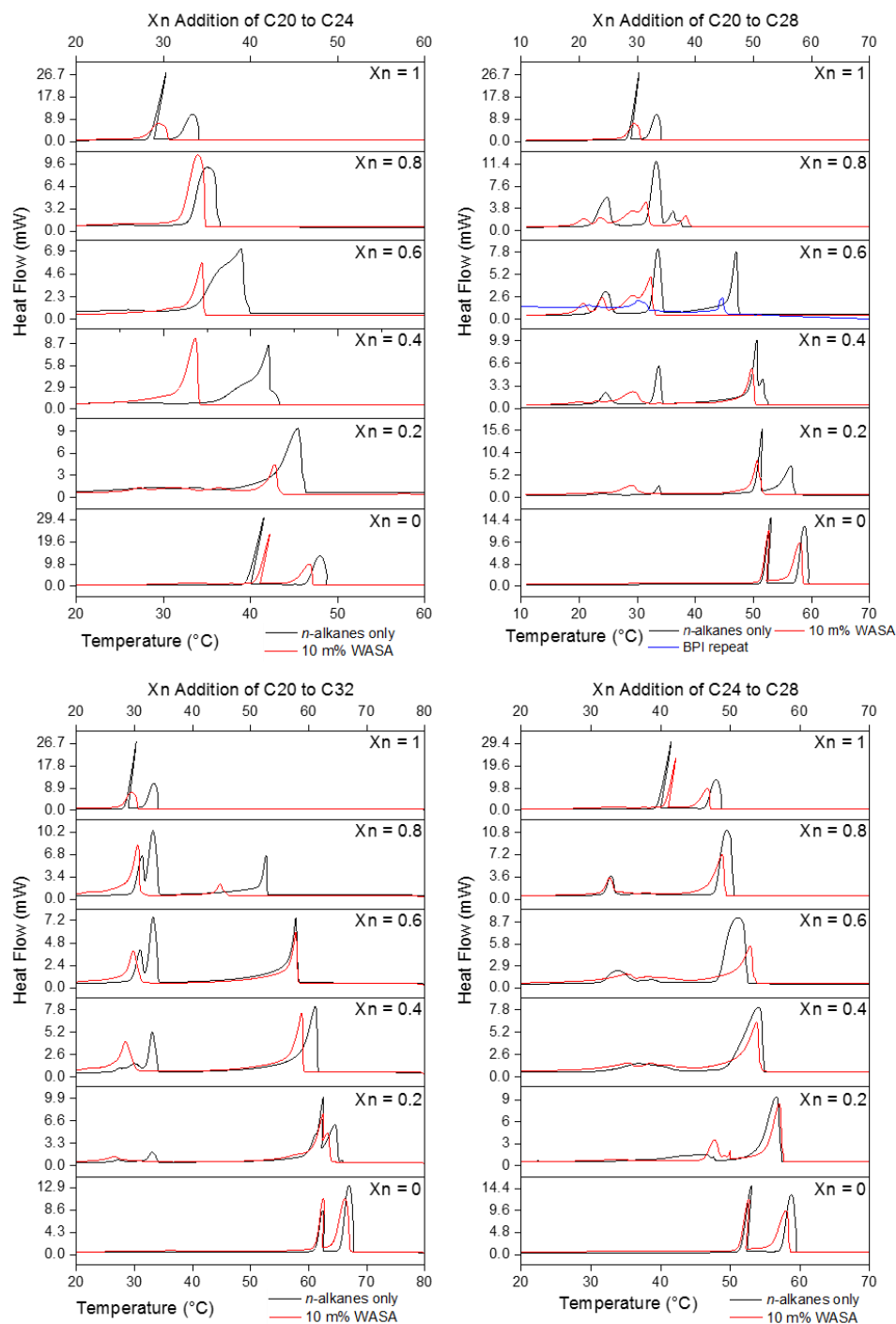


Figure 3.12: Differential scanning calorimetry cooling trace of combinations of alkanes (shown in black) and WASA (shown in red). From left to right top to bottom the graphs show the DSC traces of C₂₀ with increasing amounts of C₂₄, C₂₀ with increasing amounts of C₂₈, C₂₀ with increasing amounts of C₃₂ and C₂₄ with increasing amounts of C₂₈.

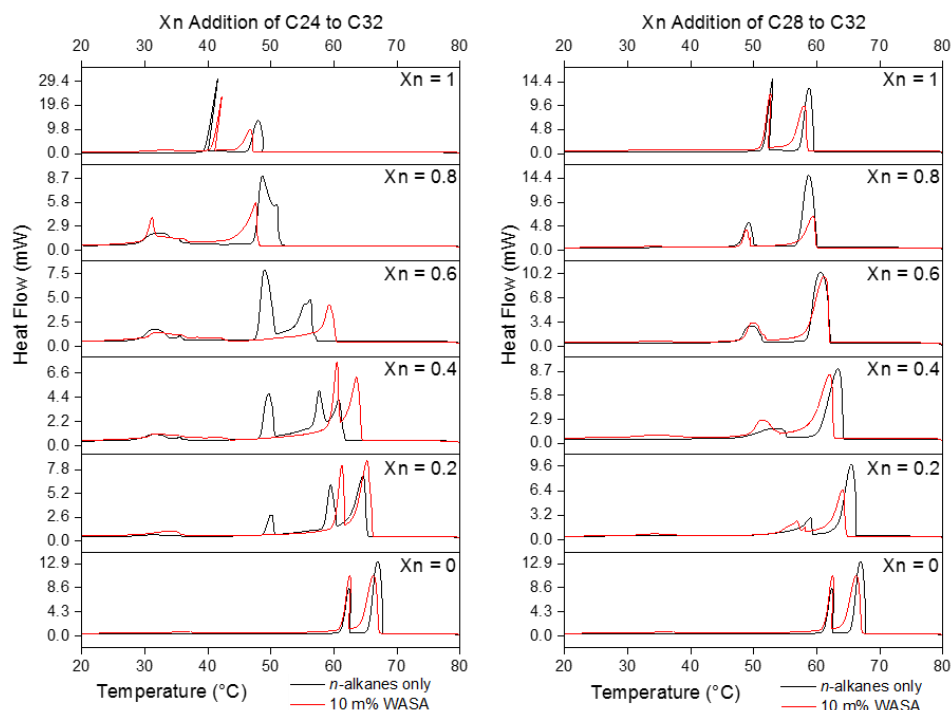


Figure 3.13: Differential scanning calorimetry cooling trace of combinations of alkanes (shown in black) and WASA (shown in red). From left to right C_{24} with increasing amounts of C_{32} and C_{28} with increasing amounts of C_{32} .

The C_{20}/C_{24} , C_{24}/C_{28} and C_{28}/C_{32} DSC traces only show one main crystallisation peak. The C_{20}/C_{28} , C_{20}/C_{32} and C_{24}/C_{32} DSC traces show two crystallisation peaks one from each n -alkane in the system. The peak heights correlate to the amount of each n -alkane in the sample. This indicates that the n -alkanes with only four carbons chain difference form co-crystals, while mixtures with chain lengths more than four carbons difference gave two distinct crystallisation peaks and do not form co-crystals.

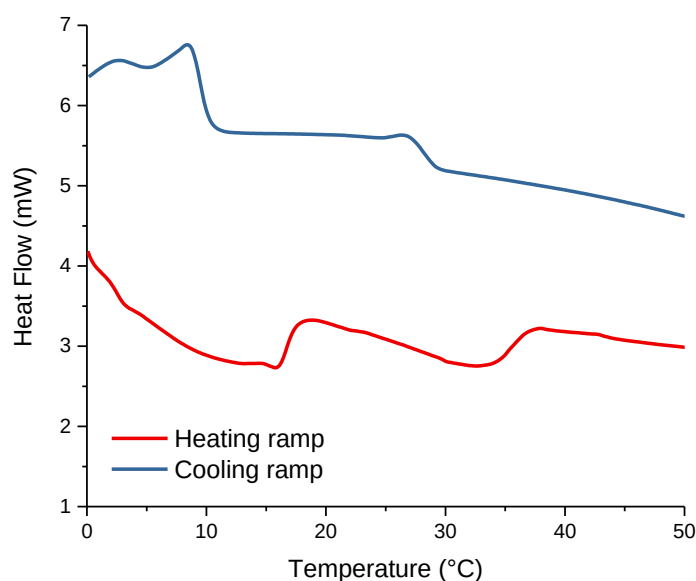


Figure 3.14: DSC cooling and heating trace of pure WASA

Figure 3.14 shows the pure WASA DSC heating and cooling traces. It shows crystallisation onset peaks at 29 °C and 11 °C and melting end set peaks at 18 °C and 37 °C. This means that crystallisation peaks seen in the eutectic data between 29 to 37 °C or 10 to 18 °C could be due to WASA crystallisation.

The red DSC traces in Figures 3.12 and 3.13 show the same *n*-alkane combinations with 10 m% WASA. Most traces show a decrease in T_c in the presence of WASA. The systems with the shorter chain length *n*-alkanes show a larger T_c decrease with the WASA present. The addition of the WASA did give rise to some additional crystallisation peaks in the C₂₀/C₂₈ system. Additionally, in samples that crystallise higher than 40 °C a small broad peak can be seen at ~ 35 °C showing WASA crystallisation. This suggests that the WASA does not co-crystallise well with the longer *n*-alkanes.

The eutectic model given in section 1.8.1 was used to calculate and plot theoretical eutectic curves using the literature values shown below in Table 3.5.

Table 3.5: Table showing the literature values used to model the eutectic point

<i>n</i>-alkane	T_m° (K)	$\Delta_{fus}H$ (kJ mol⁻¹)
C₂₀	310	68.1
C₂₄	324	53.8
C₂₈	334	63
C₃₂	343	79.7
WASA	309	3.4

The eutectic model calculated was compared with the highest melting point of each *n*-alkane mixture. Figure 3.15 shows the calculated eutectic curves and compares it to the experimentally obtained melting points of the mixtures.

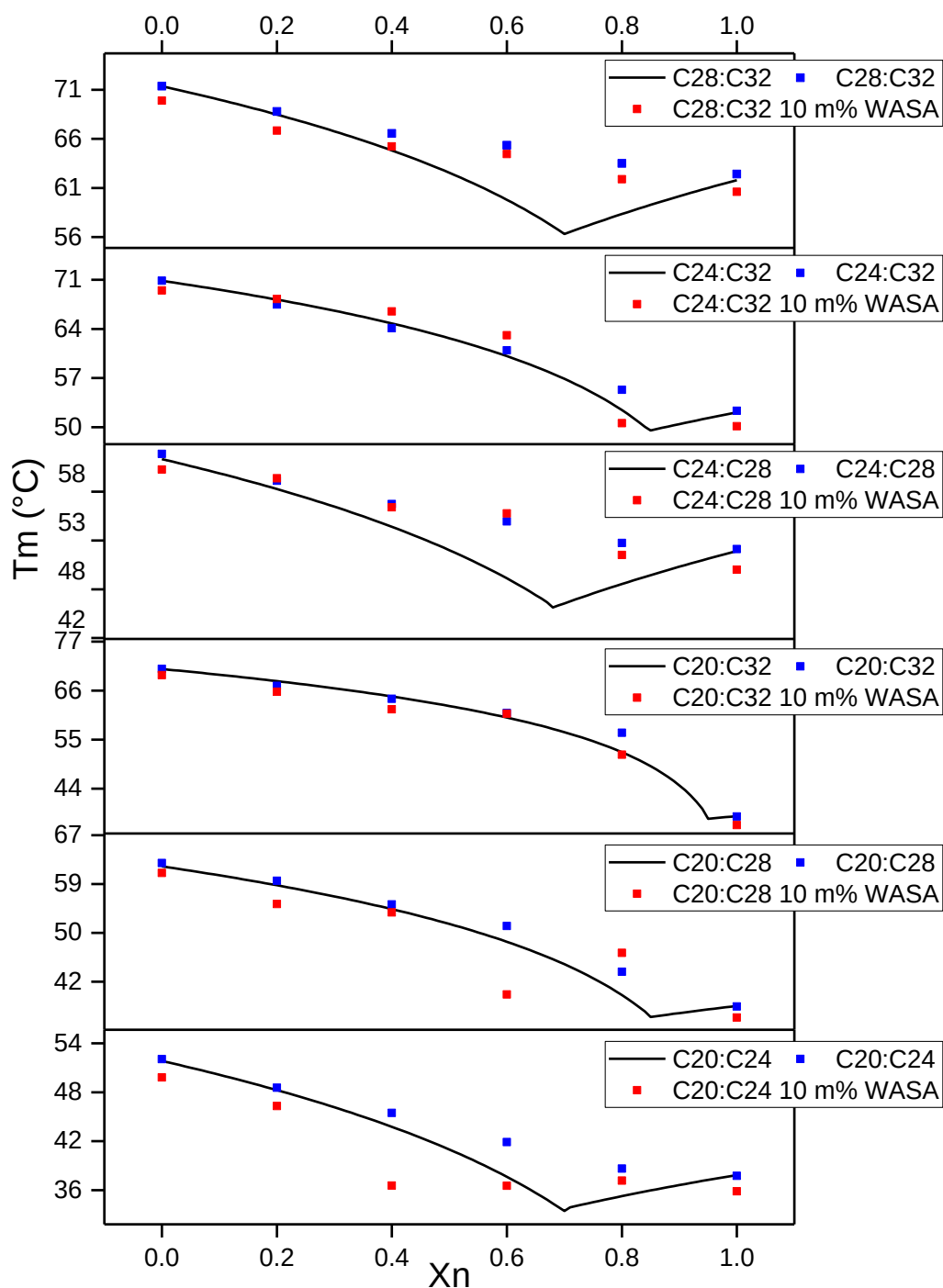


Figure 3.15: Comparison of experiment from DSC and calculated theoretical eutectic curves. The data points show the experimental data whilst the curve shows the theoretical calculation.

Some of the mixtures more closely mimic the theoretical eutectic curves than others. These mixtures, C_{20}/C_{28} , C_{20}/C_{32} and C_{24}/C_{32} , are the same mixtures that showed separate crystallisation and melting peaks in the DSC traces. The other mixtures, C_{20}/C_{24} , C_{24}/C_{28} and C_{28}/C_{32} , do not correspond as nicely with the model. This suggests that mixtures that exhibit co-crystallisation deviate more from the

eutectic model that those that do not. This is realistic as the model does not consider any co-operation between the two substances.

Upon addition of 10 m% WASA to the mixtures the melting temperature, T_m , is slightly decreased in most samples and no co-crystallisation or separation of co-crystals is induced by the WASAs presence. The average decrease in T_m upon addition of 10 m% WASA is $\sim 2^\circ\text{C}$. The eutectic model suggests that the eutectic point for WASA is over 90 m% WASA added into the n -alkanes with a melting point depression of -24°C for C_{20} , -34°C for C_{24} , -35°C for C_{28} and -38°C for C_{32} , which is unrealistic. At 10 m% added WASA the model suggests an average decrease of 1.4°C in T_m across the four n -alkanes. Comparing the model and experimental data, in Table 3.6, shows that the WASA decreased the T_m more than the model suggests. This indicates that that the decrease in crystallisation temperature seen upon addition of the WASA in the model diesel is not due to eutectic mixing.

Table 3.6: Table comparing the decrease in melting temperature observed in experimental data vs the eutectic model due to mixing 10 m% WASA into n -alkanes

n-alkane	Experimental T_m decrease ($^\circ\text{C}$)	Model T_m decrease ($^\circ\text{C}$)
C_{20}	1.9	1.2
C_{24}	2.2	1.7
C_{28}	1.7	1.5
C_{32}	1.4	1.3

3.2.3.1 Impurity in n -alkanes

The traces of single n -alkanes all show double crystallisation peaks (one of which is very sharp) but only a single melting peak (not shown above). This is not mentioned in the literature and is too sharp for a solid-solid transition. The C_{20} sample was repeated. The trace showed no change in the crystallisation and melting peaks but this sharp peak shifted a little thus, it may be due to an impurity in the Sigma Aldrich n -alkanes. Gas chromatography calibrated to detected n -alkanes specifically (run at Infineum) does not show any significant ($> 1\%$) alkane impurities. The results are shown in Figure 3.16. The nature of the impurity has not been fully established however, the bulk of the work reported is concerned with the model diesel mixture of the n -alkanes. The DSC trace of this mixture does not show unusual crystallisation peaks. In addition, impurities are very common in

petroleum diesel so the addition of impurities into the model diesel is not of great concern.

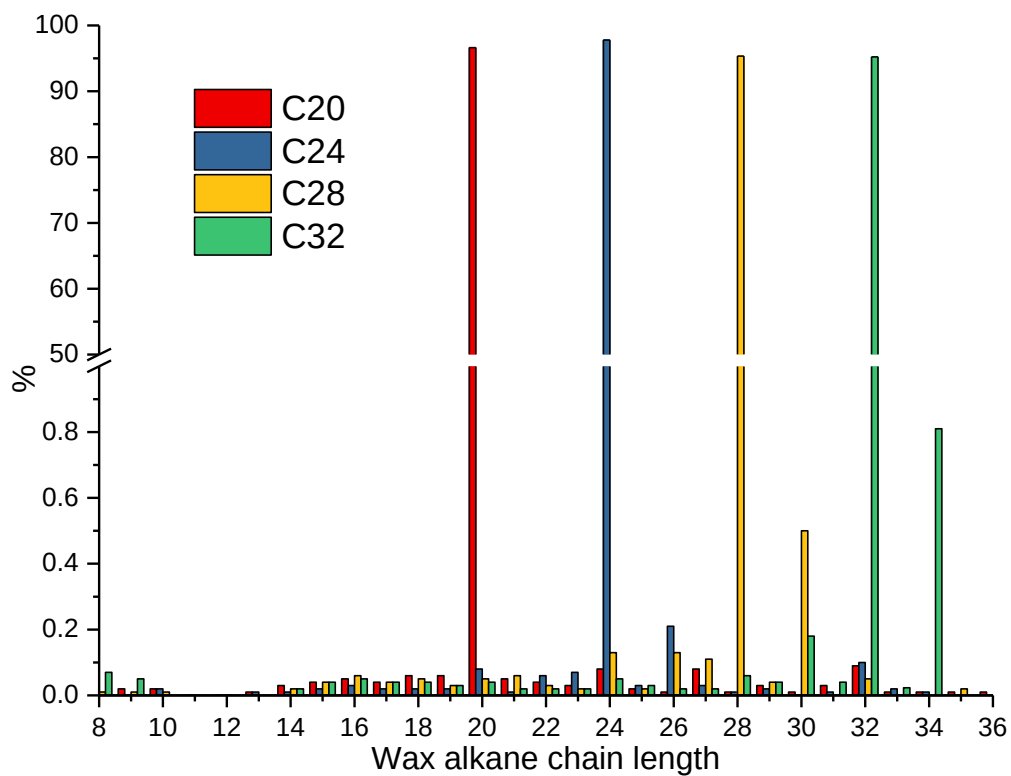


Figure 3.16: Gas chromatography of wax alkanes

3.3 Location of WASA

Ascertaining the position of WASA within the wax crystal could help to determine the mechanism of WASA action.

3.3.1 Van't Hoff

The solubility of WASA and C₂₂ FVA were compared to literature values of long chain *n*-alkanes in dodecane using the van't Hoff equation as shown in section 1.8.2.

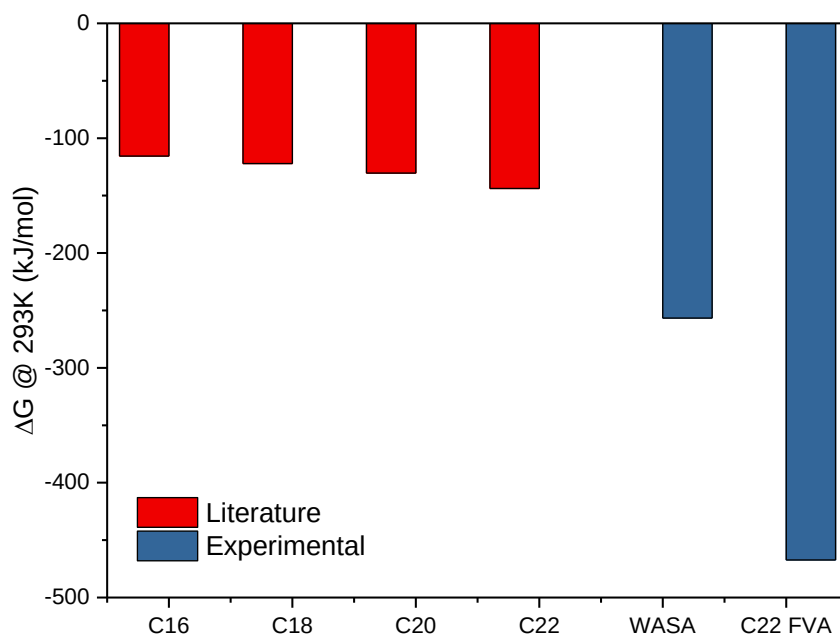


Figure 3.17: Gibbs free energy at 293K for wax alkanes from literature values and additives from experimental DSC

Figure 3.17 shows the measured Gibbs energy of crystallisation for the phase change of various pure alkanes, taken from the literature⁷² as well as the WASA and C₂₂ FVA. This data suggests that WASA and C₂₂ FVA are less soluble in dodecane than these *n*-alkanes, as the additives are thermodynamically more favourable to crystallise from the dodecane. This means that precipitated WASA and C₂₂ FVA may be present in the nucleation stage of the wax crystal growth, implying that it could be spread throughout the wax crystal rather than just present at the surface.

3.3.2 X-ray Powder Diffraction

Powdered samples of filtered and dried wax, wax with 1 wt% WASA and wax with 1 wt% C₂₂ FVA were analysed by x-ray powder diffraction. The results are shown in Figure 3.18.

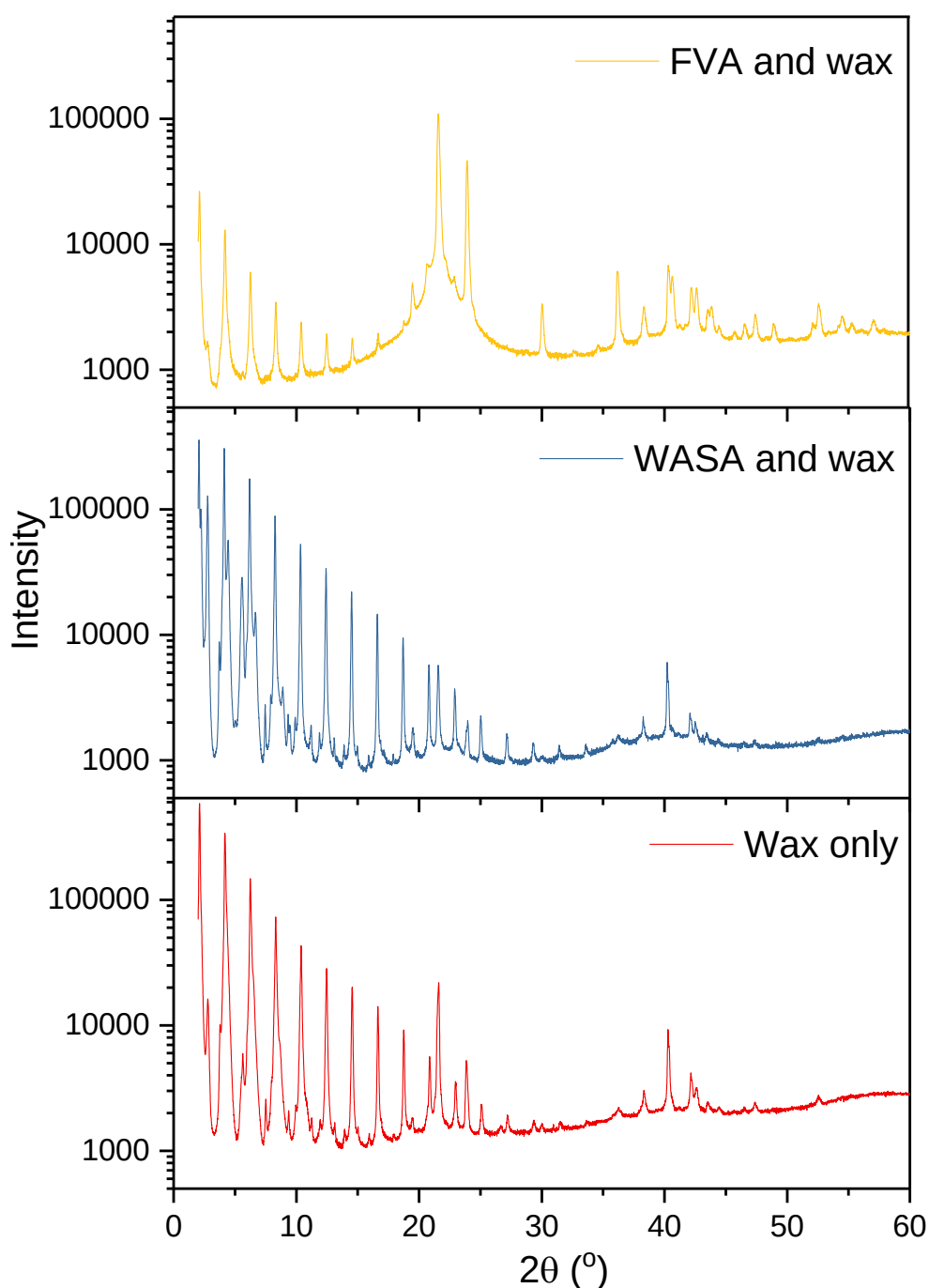


Figure 3.18: X-ray powder diffraction spectra of wax, wax with 1 wt% WASA and wax with 1 wt% C_{22} FVA

The pattern obtained for the different samples were very similar, with very little variance between peaks. This suggests that the crystal lattice is not significantly disrupted upon addition of the additives, within the limits of the instrument. From the data obtained, it is not possible to draw reliable conclusions regarding the location of the additive within the wax.

3.3.3 Infra-red spectroscopy

Wax crystals were filtered from doped and un-doped model diesel, washed thoroughly with clean dodecane and dried. Infra-red spectroscopy of WASA doped wax crystals show a peak at 1612 cm^{-1} consistent with the WASA amide stretch. Figure 3.19 shows the $1350 - 1800\text{ Hz}$ region of the IR spectra. The dashed lines show pure wax without any WASA and pure WASA. The solid lines give the wax crystals with increasing amounts of WASA. The IR spectra demonstrates that the WASA is present with the wax crystals.

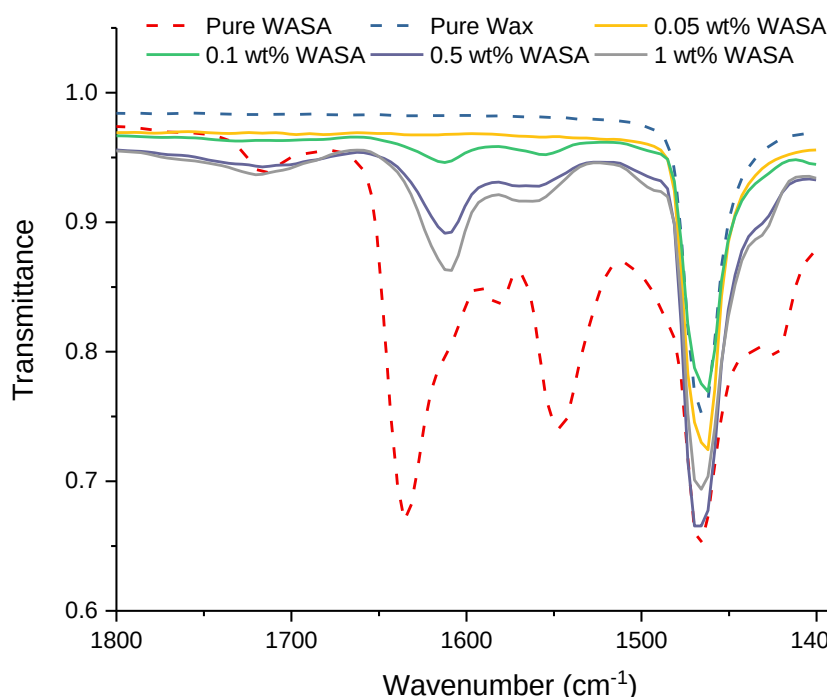


Figure 3.19: Infra-red spectroscopy of pure wax, WASA and dried wax crystals with increasing wt% amounts of WASA

3.3.3.1 ATR IR spectroscopy

To try and ascertain the extent of the WASA combination into the wax crystals several systems were compared using FT-IR spectroscopy;

1. Filtered wax – Filtered and dried wax crystals from model diesel doped with WASA.
2. Filtered dodecane – Filtered dodecane from model diesel doped with WASA.
3. Wax – *n*-alkane mixture of C_{20} , C_{24} , C_{28} and C_{32} with WASA melted together and re-solidified.
4. Dodecane – Dodecane with dissolved WASA.

These systems were doped with 0.01, 0.05, 0.1, 0.5, 1, 2.5, 5 and 7.5 wt% WASA. The FT-IR spectra of each system are shown in Figures 3.20 and 3.21. The 1612

cm⁻¹ WASA amide stretch is used to determine the presence of WASA in each system.

Figure 3.20 shows the spectra for dodecane and filtered dodecane. Neither gives a strong WASA signal but the filtered dodecane signal is weaker.

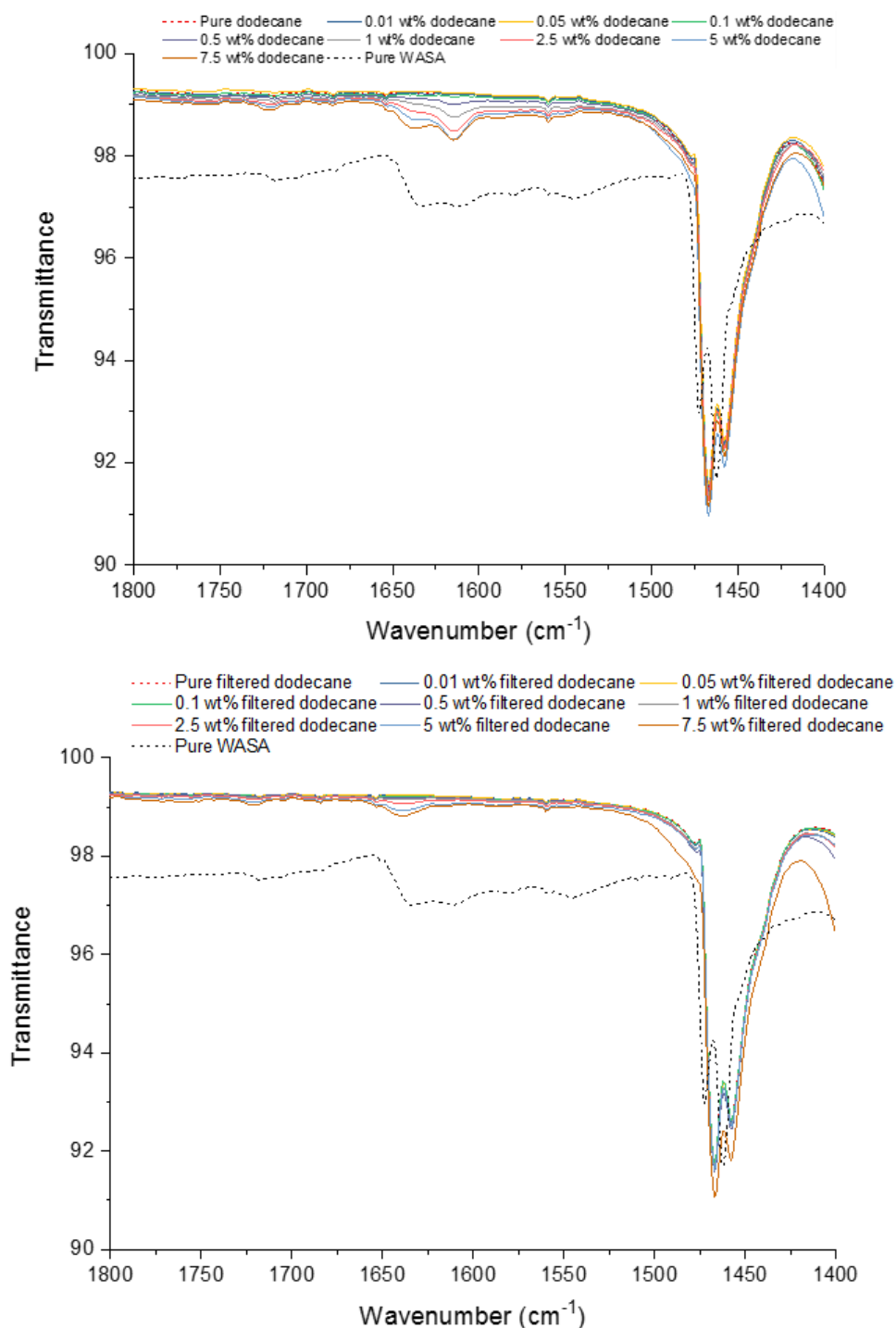


Figure 3.20: FT-IR spectra of various concentrations of WASA in dodecane (top) and WASA in dodecane that was filtered from doped model diesel (bottom).

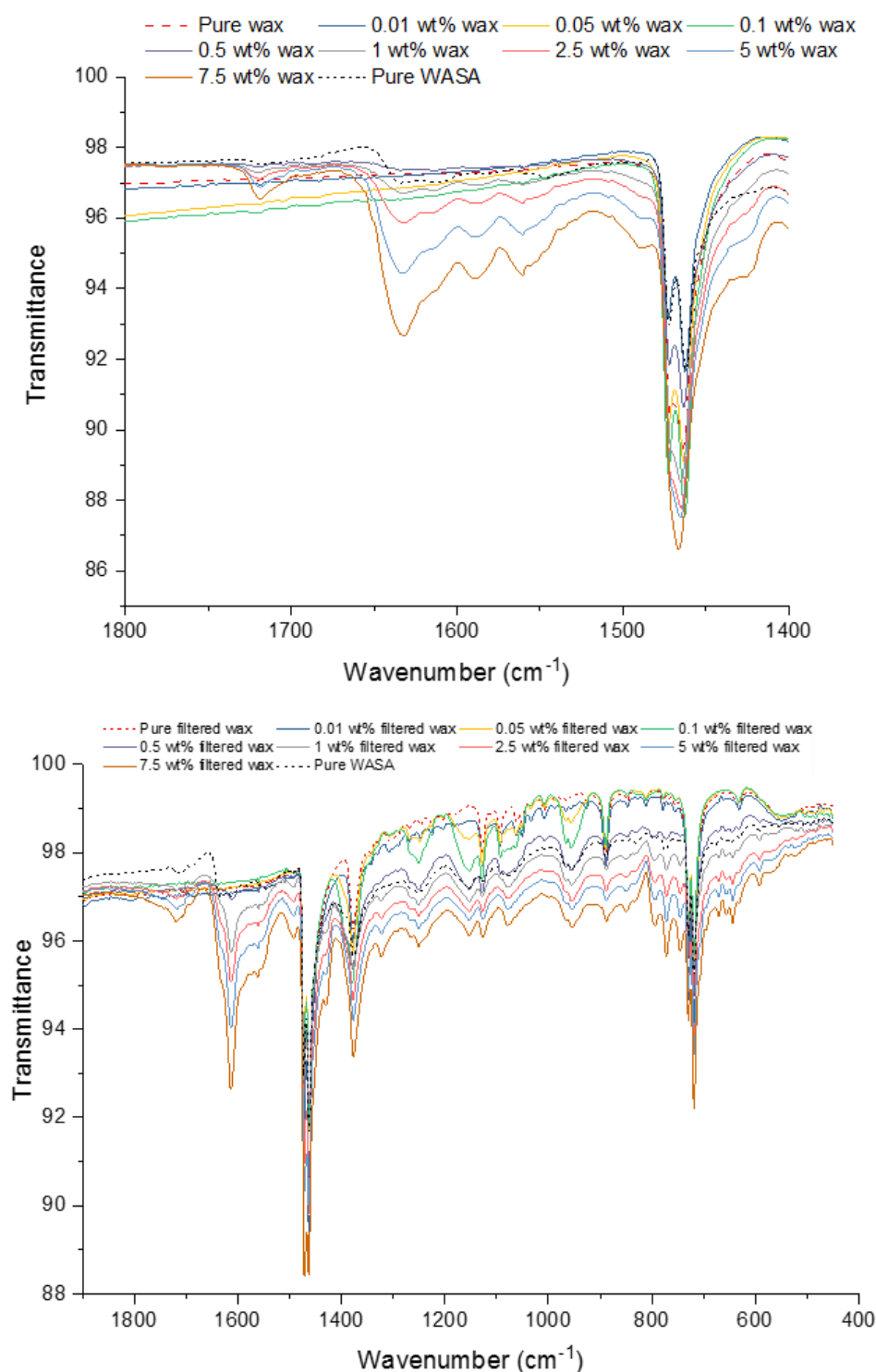


Figure 3.21: FT-IR spectra various concentrations of WASA with wax (top) and WASA doped wax that was filtered from doped model diesel (bottom).

Figure 3.21 shows the spectra for the wax and filtered wax. The 500 – 1500 cm^{-1} region peaks are associated with wax crystallisation. In the filtered wax these peaks show a broadening and decrease in intensity with increasing amounts of WASA. This implies that the wax crystals become more disordered and amorphous. Both samples have strong similar strength amide peaks.

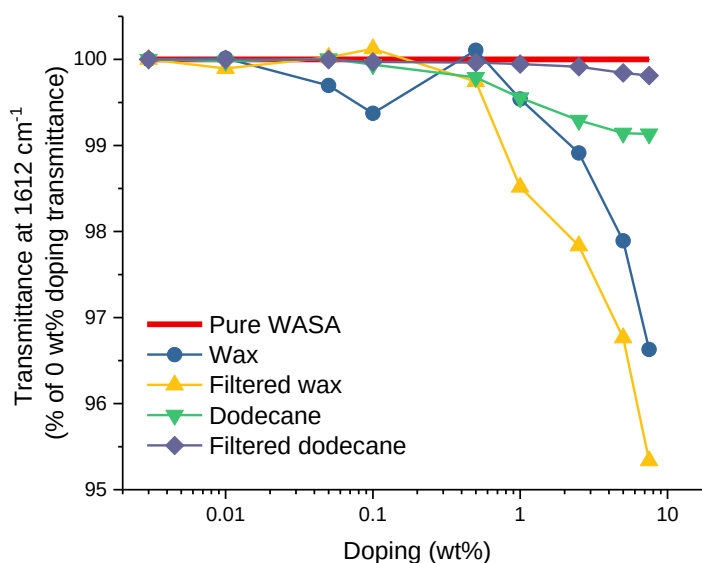


Figure 3.22: Graph showing the transmittance at 1612 cm^{-1} of the WASA doped systems as a percentage of the 0 wt% doped WASA transmittance

Figure 3.22 shows the transmittance at 1612 cm^{-1} of the WASA doped systems as a percentage of the un-doped base line transmittance of that system. It shows that the filtered dodecane shows very little WASA presence compared to the dodecane. Conversely, the filtered wax shows a stronger WASA presence than the wax. However, there is a peak shift between the WASA signals from the filtered wax and the wax melt. So they cannot be directly compared or this method used to directly calibrate the amount of WASA present in the wax.

3.3.3.2 DRIFTS IR spectroscopy

Figure 3.23 shows the IR spectra of wax and 1 wt% WASA from diffuse reflectance IR (DRIFTS-IR). Again this shows the distinctive 1612 cm^{-1} WASA amide peak implying the WASA can be found on the surface of the wax crystal. However, it is difficult to obtain a correct background for the DRIFTS-IR. The wax crystals cannot be ground up as it would disrupt their structure and thus not provide information on the WASA position. This means that the KBr powder commonly used does not give a good background. Because of this, the DRIFTS-IR and FT-IR spectra cannot be directly compared.

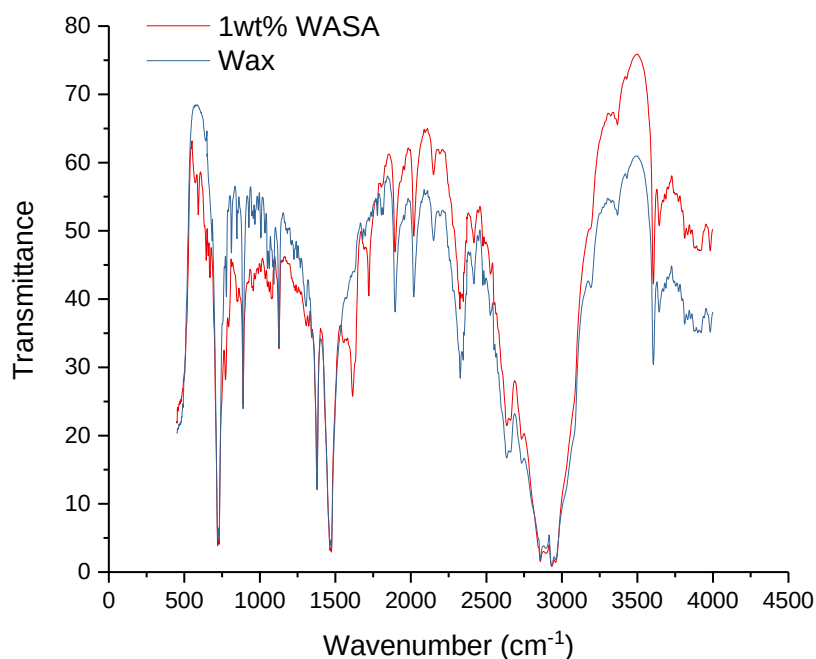


Figure 3.23: IR spectra of wax and 1 wt% WASA doped wax from DRIFTS-IR

3.3.4 X-ray photoelectron spectroscopy

Samples of filtered wax, WASA, 1 wt% WASA in wax, 2.5 wt% WASA in wax and 5 wt% WASA in wax were mounted on silicon wafers, as described in section 2.2.7. X-ray photoelectron spectroscopy (XPS) scans of the carbon, oxygen and nitrogen present in these samples were run by NEXUS. An XPS depth profile was achieved by etching for 0 to 270 seconds with spectra taken every 30 seconds. The etch rate of carbon is roughly $50 \text{ \AA min}^{-1}$.⁹¹ Figures 3.24 and 3.25 show the N1s and O1s scans with increasing etching times. The C1s scan is not shown as it did not show variance over the different samples and etching times.

Figure 3.26 shows the atomic percentage (relative to etching time 0 s) calculated from the area under the oxygen and nitrogen spectral peaks. An etching time of 270 s corresponds to a depth of roughly $225 \text{ \AA}$. The O1s scan shows a decrease in the O presence as the etching time increased. This suggests that the WASA is more prominent on the surface of the wax crystal. The N1s scan is very noisy. N is also hard to detect in XPS and gives a weak signal. Thus, the fact that the N1s scan does not mimic the O1s scans' decrease in atomic percentage does not discount the result from the O1s scan.

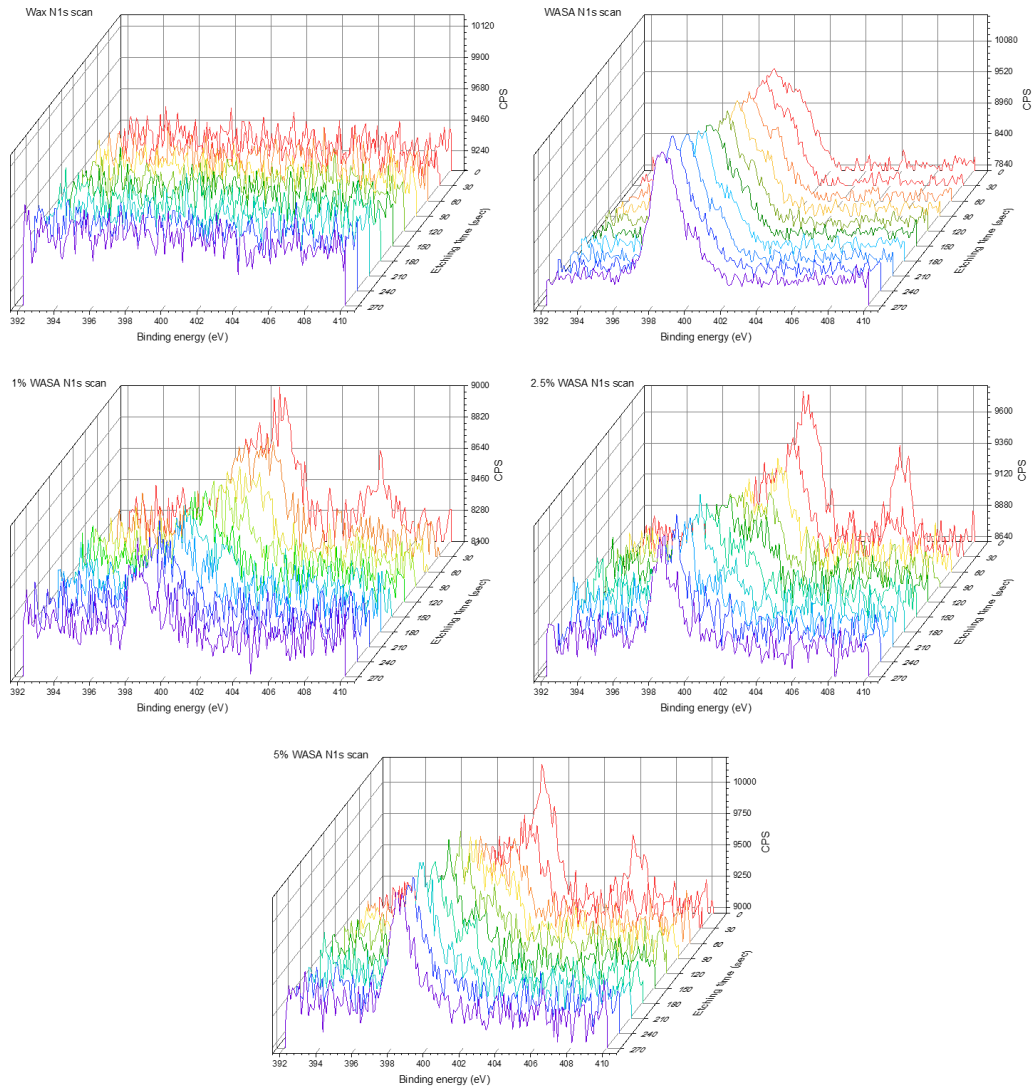


Figure 3.24: XPS etching spectra of N1s scans. From top right corner; Wax, WASA, 1 wt% WASA in wax, 2.5 wt% WASA in wax and 5 wt% WASA in wax

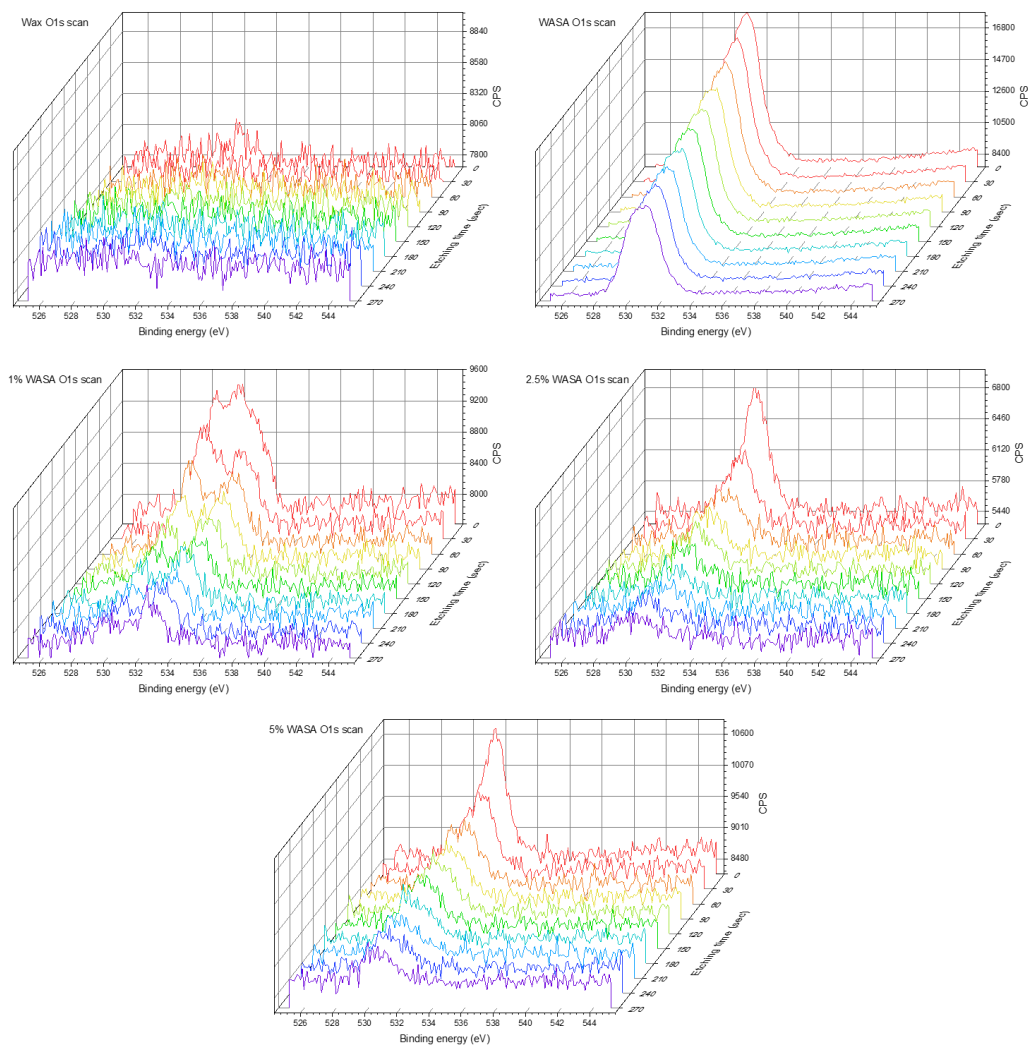


Figure 3.25: XPS etching spectra of O1s scans. Form top right corner; Wax, WASA, 1 wt% WASA in wax, 2.5 wt% WASA in wax and 5 wt% WASA in wax

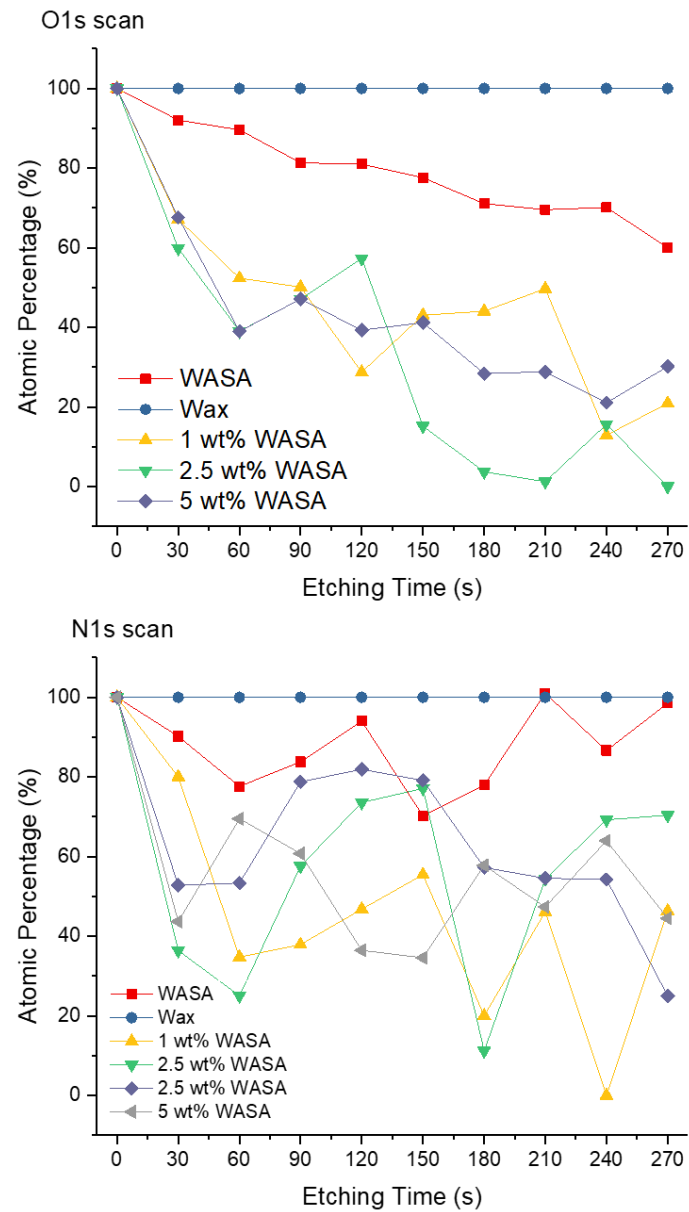


Figure 3.26: Atomic percentage vs etching time of XPS spectra from N1s and O1s scans

3.4 Other additives

Other additives and molecules were doped into the model diesel to see their effects on the wax crystals to compare to WASA. C_{22} FVA, AOT and two ionic liquids, $PC_4.Cl^-$ and $[Bmim][NtF_2]$, were doped into model diesel at 0.05 wt%, 0.1 wt%, 0.5 wt% and 1 wt%. C_{22} FVA was used because it is an industrially used cold flow additive that decreases the wax crystal size. AOT was used because it is a common long chain surfactant with alkane chain lengths similar to WASA. The ionic liquids were used to mimic the salt like nature of WASA but with a lower dissociation energy, additionally $[Bmim][NtF_2]$ has long alkane side chains. The effect of these additives on the appearance, crystallisation temperature and IR spectra of the wax crystals was tested, similar to section 3.2.1.

3.4.1 Optical Microscope images

Optical microscope images of the additives and WASA doped at 1 wt% are shown in Figure 3.27.

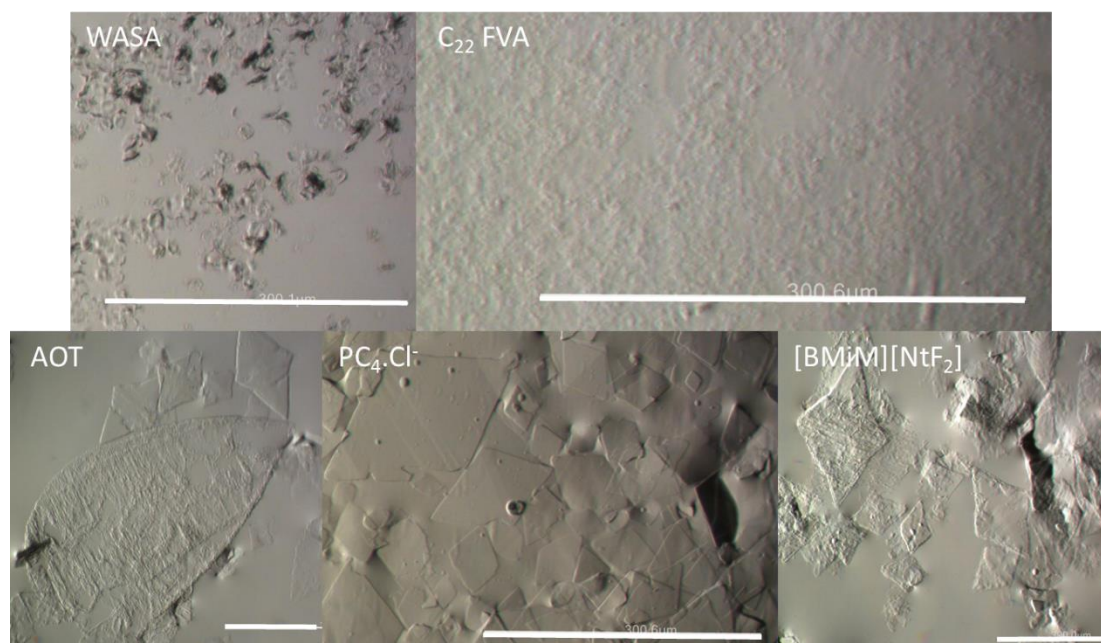


Figure 3.27: Microscope images of 1 wt% doped WASA, C_{22} FVA, AOT, $PC_4.Cl^-$ and $[Bmim][NtF_2]$. White bar indicates 300 μm .

In agreement with results seen in section 3.2.1.1, WASA and C_{22} FVA decrease the wax crystal size. C_{22} FVA decreases the wax crystals size more than that of WASA and both change the crystal morphology to a small cuboid shape. AOT and ionic liquids $PC_4.Cl^-$ and $[Bmim][NtF_2]$ do not reduce the crystal size nor change the crystal morphology.

3.4.2 Differential scanning calorimetry

Differential scanning calorimetry (DSC) cooling traces of the additives and WASA doped at 1 wt% are shown in Figure 3.28.

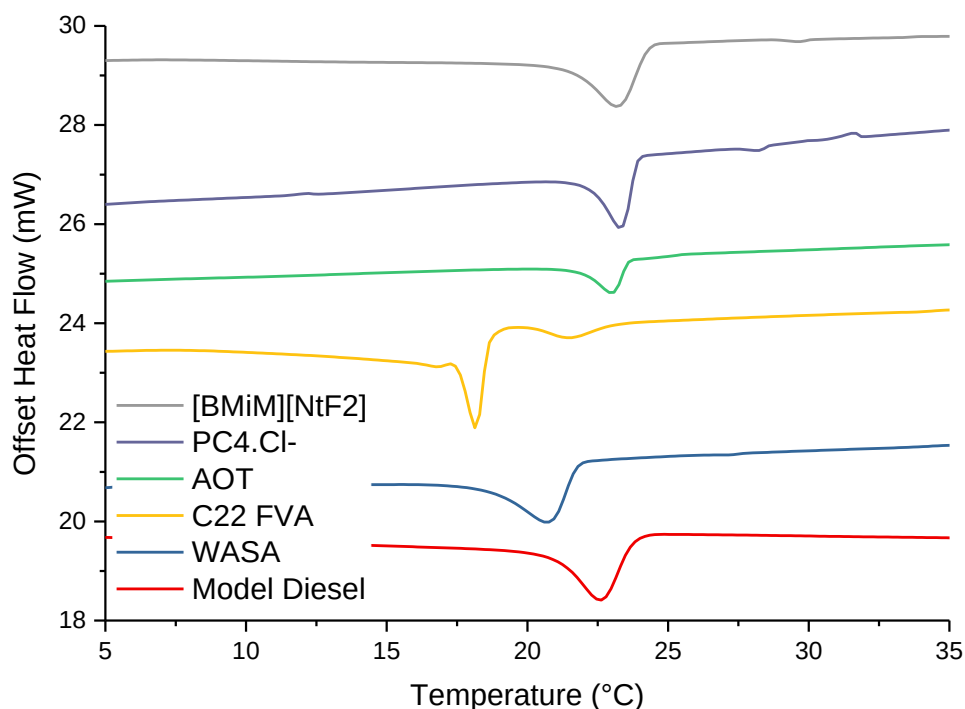


Figure 3.28: Differential scanning calorimetry cooling trace of model diesel and model diesel with 1 wt% doped WASA, C₂₂ FVA, AOT, PC₄.Cl⁻ and [BMiM][NtF₂].

At 1 wt%, WASA reduced the wax crystallisation temperature by -2 °C and C₂₂ FVA by -7 °C. AOT, PC₄.Cl⁻ and [BMiM][NtF₂] did not affect the crystallisation temperature.

3.4.3 Infra-red spectroscopy

Wax crystals from model diesel doped at 0.05, 0.1, 0.5 and 1 wt% with the various additives were filtered, washed extensively with dodecane and left to dry. The IR spectra of these additives, pure wax crystals and the doped wax crystals were obtained via ATR-IR.

Pure C₂₂ FVA gives two distinct C-O ester stretches at 1200 cm⁻¹. Pure wax does not have any peaks in this region, so they are diagnostic peaks for the presence of C₂₂ FVA in the wax crystals. All doped waxes show the presence of the C₂₂ FVA with 1 wt% and 0.5 wt% showing strong ester peaks. This indicates that C₂₂ FVA is present on the wax crystals as shown in Figure 3.29.

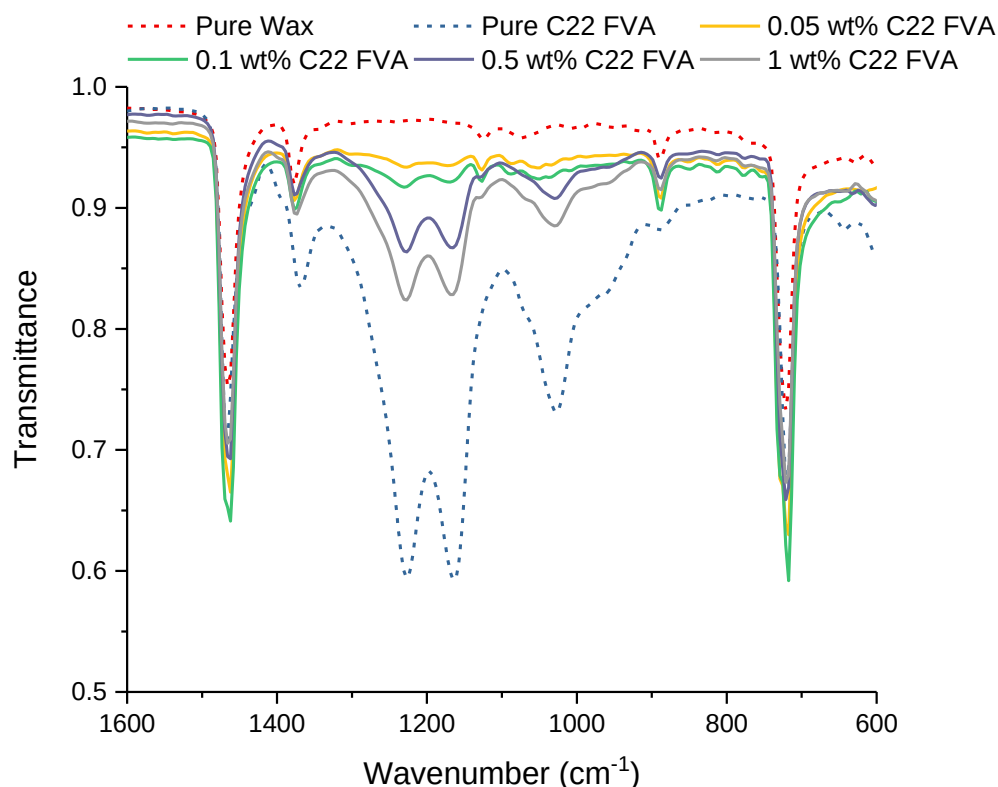


Figure 3.29: IR spectra of pure wax, pure C₂₂ FVA and C₂₂ FVA doped filtered, washed and dried wax crystals.

The IR spectra of wax crystals doped with ionic liquids PC₄.Cl⁻ and [BMiM][NtF₂] show very little presence of the ionic liquids, shown in Figure 3.30. [BMiM][NtF₂] gives IR bands at 1049 cm⁻¹ (S=O bending), 1250–1100 cm⁻¹ (C–F stretching), 1342 cm⁻¹ (C=C stretching) and 1573 cm⁻¹ (C=N stretching).⁹² These bands can be weakly seen in the 1 wt% and 0.5 wt% doped wax crystals however upon further washing the bands strength decreased. This implies, along with the DSC results, that the ionic liquids do not strongly interact with the wax crystals.

Similarly, pure AOT gives a strong C=O ester band at 1728 cm⁻¹ and strong C–O ester bands around 1200 cm⁻¹. 1 wt% AOT doped wax shows no bands in these regions indicating that AOT is not present on the wax crystals shown in Figure 3.30.

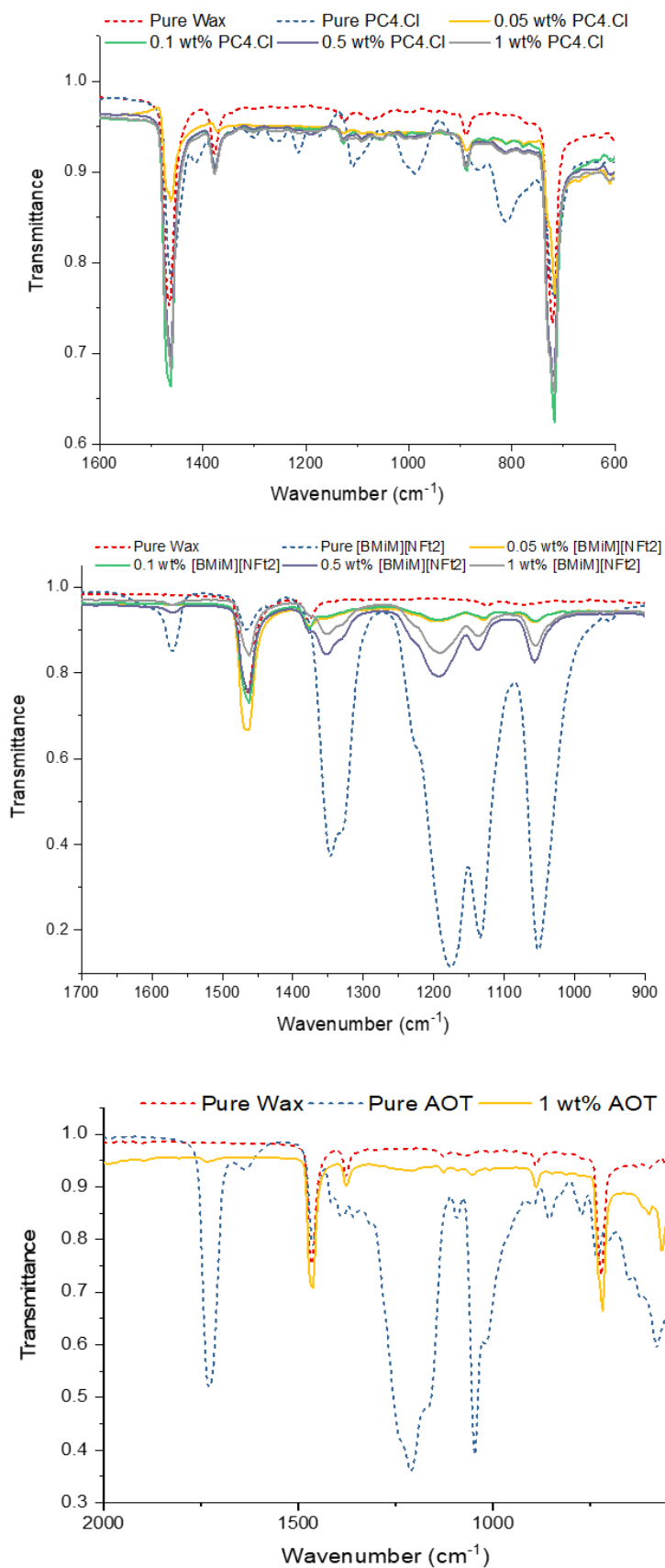


Figure 3.30: IR spectra of pure wax, pure PC₄Cl (top), [BMiM][NtF₂] (middle) and AOT (bottom) and PC₄Cl (top), [BMiM][NtF₂] (middle) and AOT (bottom) doped filtered, washed and dried wax crystals

4 Results – How Does Anti-Settling Occur?

The previous chapter discussed development of the model diesel, the effect of WASA on the model diesel and its location in the wax crystals. This chapter deals with trying to elucidate the mechanism of the WASA's wax anti-settling action seen in petroleum diesel.

4.1 Electrophoresis

Charged species in petroleum species have been previously observed; Weitz⁵⁹ has shown electrophoretic mobility of soot particles within marine fuel. This inspired our investigation of electrostatic stability of wax crystals by the WASA. The experimental set up and protocol for these electrophoresis experiments are described in section 2.2.8.

4.1.1 Glass electrophoresis cell

The initial electrophoresis experiment was conducted in a glass round bottomed electrophoresis cell (Figure 4.1). The electrodes were placed 2 cm apart and the voltage ramped up to 2500 V and held for 5 minutes. During this 0 mA and 0 W were shown on the Consort EV233 power supply. The cell was loaded with model diesel doped with 1 wt% WASA.

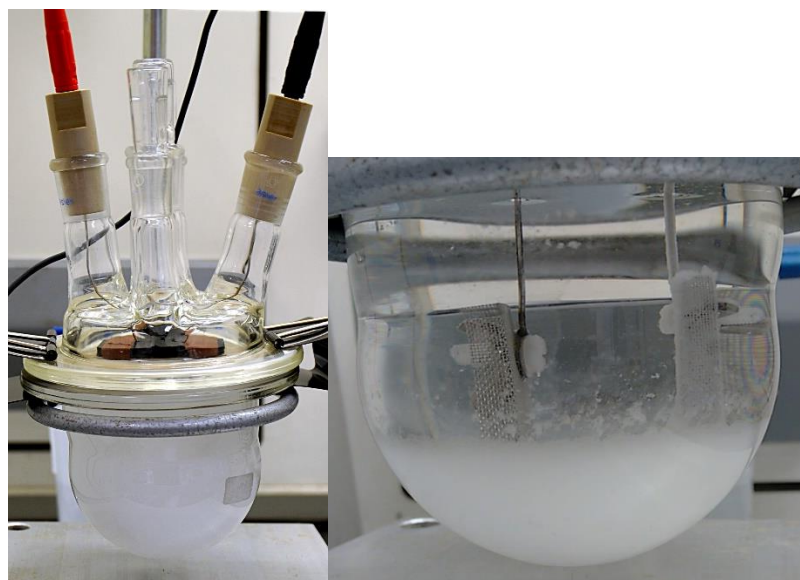


Figure 4.1: Left – initial electrophoresis set up at beginning of test. The black right electrode is the negative cathode and the left red electrode is the positive anode. Right – end of electrophoresis test showing wax crystals doped with 1 wt% WASA collecting on cathode.

Figure 4.1 shows the result of this initial test. The wax crystals collected on the cathode and settled. This indicates that the wax crystals are positively charged.

The round bottomed cell is not ideal for taking pictures due to reflections. Thus, a second rectangular cell was designed and built.

4.1.2 Perspex electrophoresis cell

The rectangular cell with a backlight gives a better contrast for viewing the wax crystals the positive anode is on the left and the negative cathode is on the right, as shown in Figure 4.2.

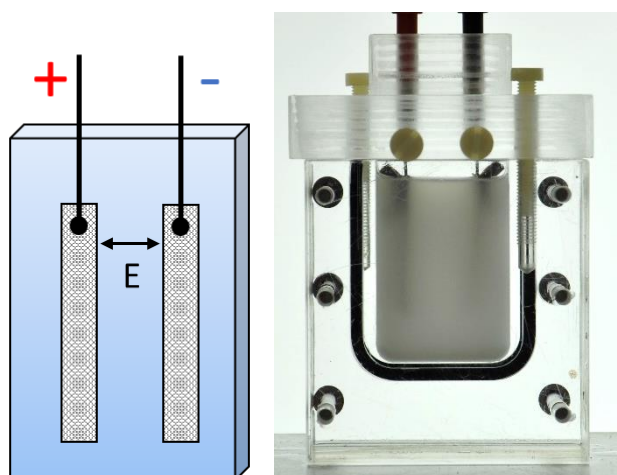


Figure 4.2: Diagram and picture of initial electrophoresis set up at beginning of test left electrode is the anode and right electrode is the cathode

To test the cell, it was charged with a 0.68 wt% latex in water mixture, enough so that the latex is clearly visible but not enough so that the solution is opaque. The voltage was ramped to 30 V and held for 5 minutes. The electrodes were placed 2 cm apart. The latex particles were 120 nm in size and showed a mobility of $-3.6 \text{ } (\mu\text{m s}^{-1})/(\text{V cm}^{-1})$ and zeta potential of -50.68 mV as measured in a Brookhaven ZetaPALS.



Figure 4.3: 0.68 wt% latex in water mixture.

In Figure 4.3 the electrophoresis of the latex in water showed the latex repelled from the negative cathode and attached to the positive anode. This result agrees with the zeta potential measurements.

The cell was charged with 1 wt% WASA doped model diesel. The electrodes were placed 2 cm apart and the voltage ramped up to 2500 V over one minute and held for 5 minutes. Initially the cell was filled to above the electrodes in case of arcing. However, the wingnuts also became charged. Subsequently the cell was filled with roughly 30 ml of sample to below the wingnuts (Figure 4.4, image 4).

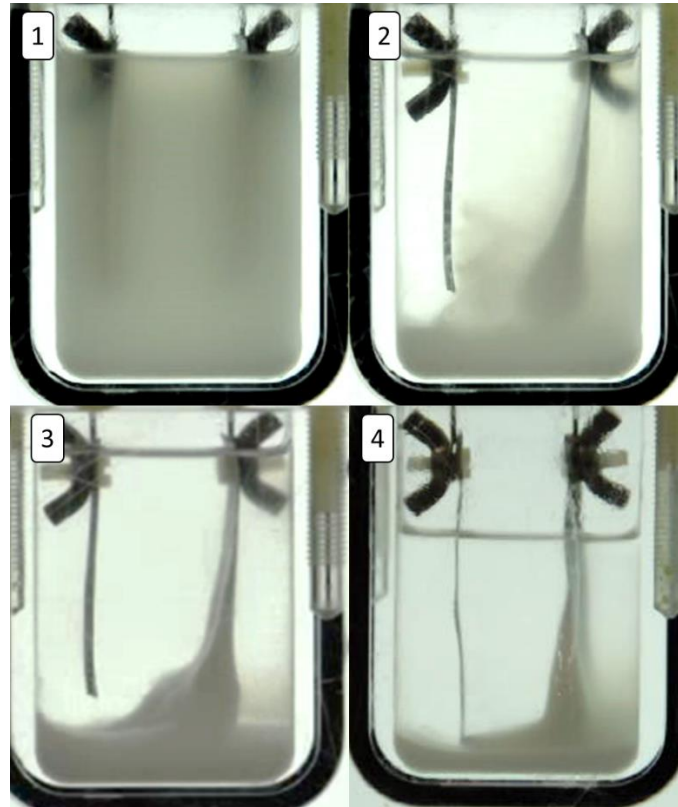


Figure 4.4: Model diesel doped with 1 wt% WASA model diesel. 1) cell at beginning of test, 2) cell at 2500V, 3) cell at the end of the test and 4) a repeated test cell.

Figure 4.4 shows photos of 1 wt% WASA doped model diesel. During the initial ramping to 2500 V the wax crystals near the anode are repelled with the crystals between the anode and the cell wall settling quickly. Crystals between the cathode and anode are attracted towards the cathode. However, the electrophoretic motion is not a simple direct motion. The crystals settle and some seem to be attracted towards the anode and then quickly repelled again. This can be seen in photo 2 of Figure 4.4 in the wax cloud fingers towards the anode. The majority of the crystals are attracted towards and gather on the cathode or settle on the bottom of the cell. This test was repeated with a new sample with the same result. This suggests that the WASA is imparting a positive charge to the wax crystals.

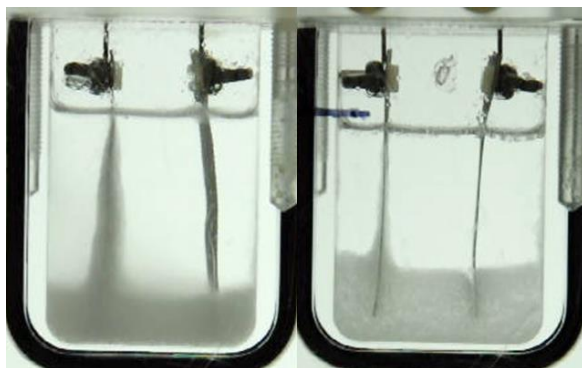


Figure 4.5.: Photos shows different tests on same un-doped model diesel at the end of the test.

Figure 4.5 shows photos at the end of the test of un-doped model diesel. The wax crystals are weakly attracted to the anode. This is surprising as there are no additives present in the diesel. One possible explanation of this is that there might be impurities present in the system.

4.1.2.1 Drying model diesel

The model diesel used in Figure 4.5 was treated with a de-ionised water shake and then dried with CaCl_2 . The model diesel was hot filtered at 80°C to remove the CaCl_2 but preserve the melted wax. Any excess water was removed *via* a separating funnel. The dried model diesel was left to recrystallise and then retested in the electrophoresis cell.

Figure 4.6 shows the end of the electrophoresis test of the dried model diesel. There is no longer a strong attraction to either electrode. This suggests that the previous attraction to the anode might be due to water or impurities which were removed by the de-ionised water shake and CaCl_2 drying.

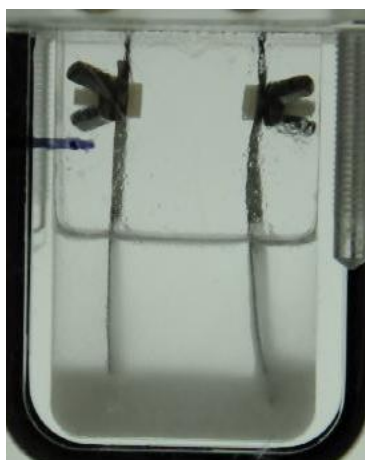


Figure 4.6: Dried model diesel

4.1.2.2 Changing the WASA amount

The amount of WASA doping was reduced to 0.01 wt% and the electrophoresis test repeated. Figure 4.7 shows the end of this test. The majority of crystals are attracted towards and gather on the cathode or settle on the bottom of the cell. Again this suggests that the WASA is imparting a positive charge to the wax crystals even with low amounts of WASA.



Figure 4.7: Model diesel doped with 0.01 wt% WASA model diesel.

4.1.2.3 C₂₂ FVA effect

To compare the electrophoretic effect of WASA with other additives, the model diesel was doped with 1 wt% C₂₂ FVA and tested in the cell. Figure 4.8 shows the end of the electrophoresis test at 2500 V. The C₂₂ FVA doped model diesel showed no attraction to either electrode. This suggests that the C₂₂ FVA does not impart any charge to the wax crystals. This is particularly interesting as the non-ionic C₂₂ FVA is not used as an anti-settling additive, suggesting there may be a link between charge and anti-settling effect.

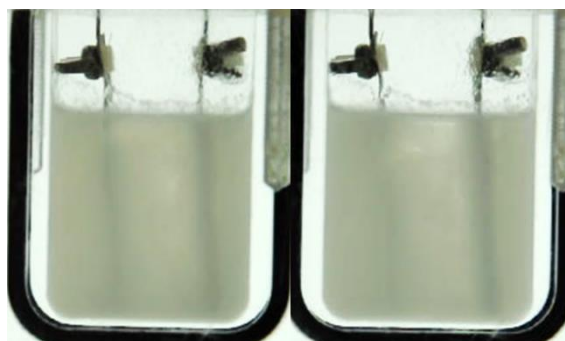


Figure 4.8: Two pictures of model diesel doped with 1 wt% C₂₂ FVA repeated.

Combinations of cold flow additives are often used in formulations, to improve several aspects of the diesel performance. Therefore, to emulate this the model diesel was doped with 1 wt% of both WASA and C₂₂ FVA.

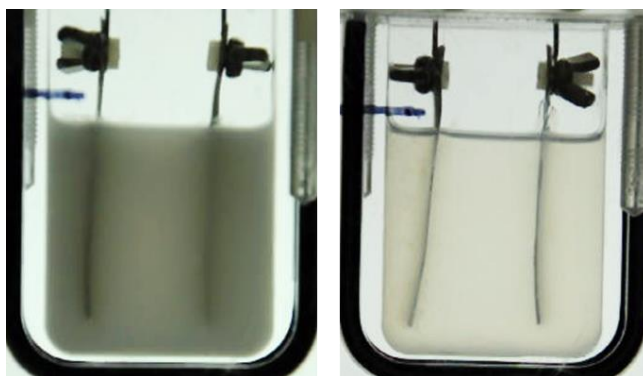


Figure 4.9: Left – 1 wt% of each WASA and C₂₂ FVA in model diesel. Right – 1 wt% of each WASA and C₂₂ FVA in model diesel diluted with dodecane by half.

Figure 4.9 shows the end of the electrophoresis test at 2500 V. The model diesel doped with equal amounts of WASA and C₂₂ FVA gave no attraction to either electrode. The sample was diluted by half with dodecane to view the movement of the wax crystals more clearly; again no electrophoretic mobility was observed.

4.1.2.4 Changing the voltage

Testing was conducted on 1 wt% WASA doped model diesel at different voltages to gauge the strength of the effect.

Table 4.1: Results of electrophoresis of 1 wt% WASA model diesel at different voltages

Voltage (V)	Effect on wax crystals
30	None observed.
50	Weak repulsion from the anode.
100	Weak repulsion from the anode.
200	More pronounced repulsion from the anode.
500	Strong repulsion from the anode.
700	Strong repulsion and repulsion induced settling from the anode. Attraction to and collection on the cathode.
1000	Strong repulsion and repulsion induced settling from the anode. Strong quick attraction to and collection on the cathode.

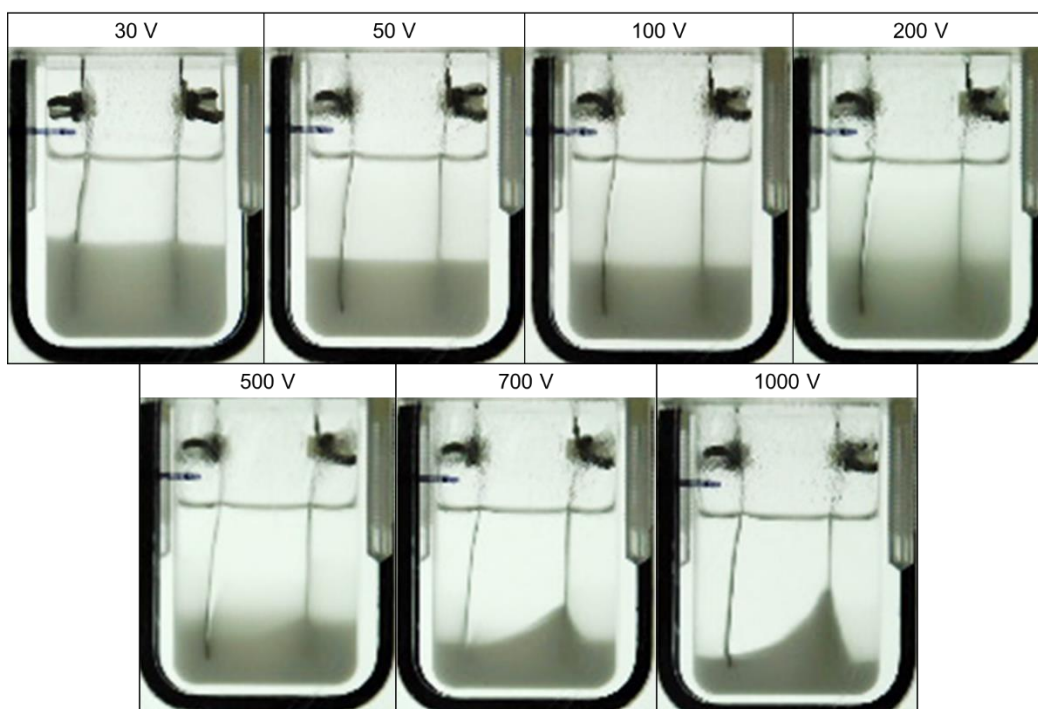


Figure 4.10: Pictures of 1 wt% WASA model diesel at the end of the electrophoresis test to varying voltages.

Table 4.1 and Figure 4.10 show the results of the electrophoresis test of 1 wt% WASA doped model diesel at different voltages. A weak electrophoretic effect is seen as low as 50 V and becomes dramatic at 200 V and higher.

4.1.2.5 Organic salt addition

An organic salt, tetrabutylammonium bromide, was added to the 1 wt% WASA doped model diesel. This was done to see if it screened the charge from the WASA and thus reduced the electrophoretic effect. The sample was run at several voltages to be able to compare to section 4.1.2.4. Table 4.2 and Figure 4.11 show the results of the electrophoresis tests.

Table 4.2: Results of electrophoresis of 1 wt% WASA model diesel and organic salt at different voltages.

Voltage (V)	Effect on wax crystals
30	None observed.
50	None observed.
100	Weak repulsion from the anode.
200	More pronounced repulsion from the anode. No observed collection on the cathode.
500	Strong repulsion from both electrodes but more so from anode. The crystals seem to be pushed to the sides of the cell.

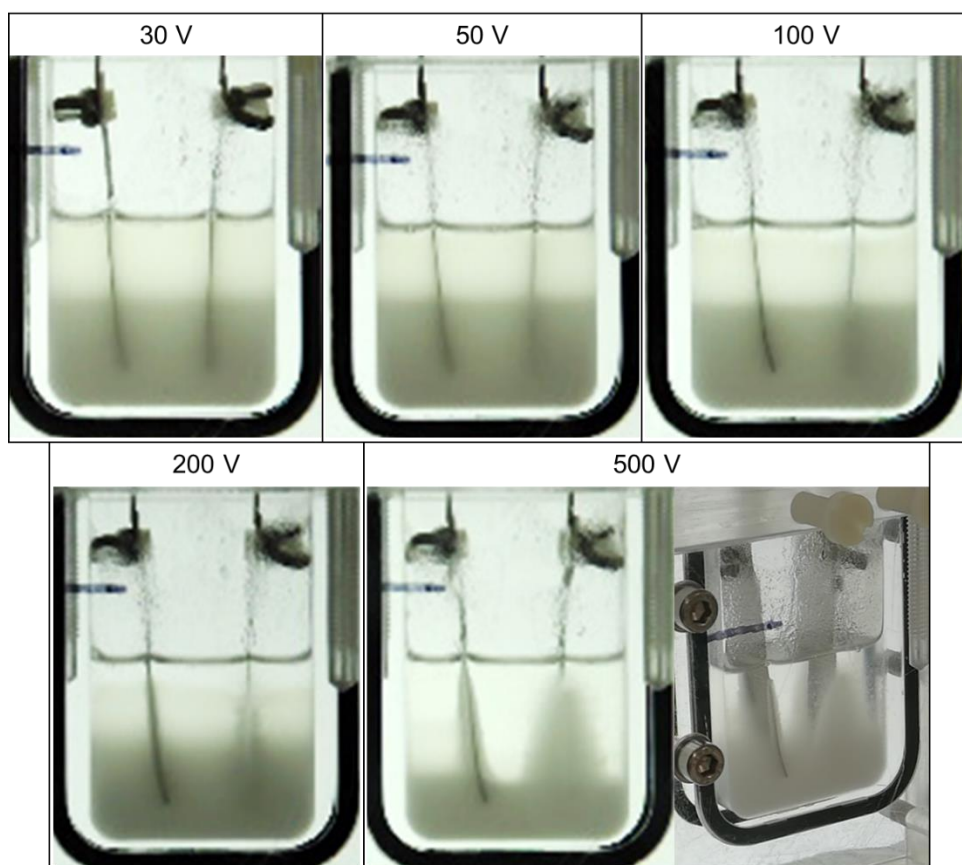


Figure 4.11: Pictures of 1 wt% WASA model diesel and organic salt at the end of the electrophoresis test to varying voltages.

A weak electrophoretic effect is first seen at a higher voltage of 100 V compared to the previous sample with no organic salt. Additionally, the wax crystals seem slightly repelled from the anode. At 500 V we can observe from the side angle picture that the wax crystals do not collect on either electrode and are repelled to the side of the cell. This shows that the organic salt is effective in screening the charge imparted to the wax crystals from the WASA.

4.1.3 Conductivity

The conductivity of 1 wt% WASA in pure dodecane was tested with a conductivity probe with a detection limit of $0.01 \mu\text{S}$. Over a temperature range of 15 to 40°C the conductivity was $0.02 \pm 0.01 \mu\text{S}$. Over the same temperature range undoped dodecane had the same conductivity.

A more sensitive conductivity probe was required to measure non-aqueous systems. Acros anhydrous dodecane was purchased and dried with $14 \text{ \AA}$ molecular sieves. Samples of WASA in this dried dodecane were made up at various concentrations and sent to Bristol University for more sensitive testing.

Each sample was tested three times to give error bars, shown in Figure 4.12. Analytical standard Sigma-Aldrich dodecane was also tested for comparison.

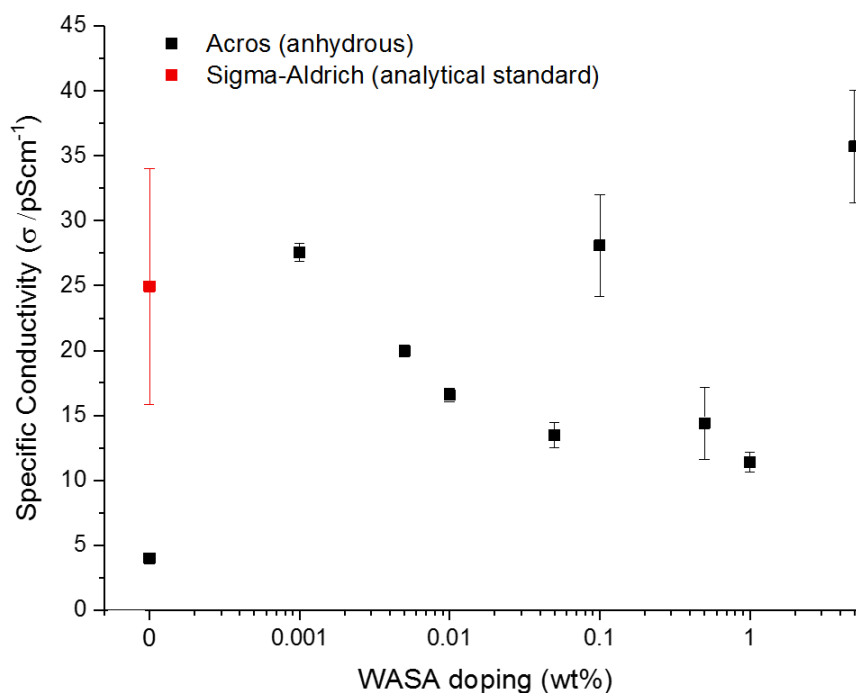


Figure 4.12: Graph showing the specific conductivity vs the wt% of WASA in the dodecane.

As the WASA wt% increased the specific conductivity measured also increased, however not in a proportional or direct manner. Most of the samples were also within the error bars of the analytical standard Sigma-Aldrich dodecane used in the model diesel.

4.2 Rheology

Anti-settling can be caused by a weak gel. Thus, we decided to study the model diesel gelation by rheology to hopefully reveal insight into the gel. We can then compare this to doped systems to see how additives change the gel. The theory behind and method for these experiments is described in section 2.2.10.

4.2.1 Creep and oscillatory rheology

Previous literature showed the use of oscillatory rheology as a method to study these systems.⁹³ Initial work on a Bohlin Rheometer gave noisy data with the expected linear viscoelastic region not clearly defined. This raised concerns of wall slip and the possibility that the wax crystals were aligning themselves to the geometries' surface and causing the instrument to not measuring the true bulk rheology of the system.

To address this, a mould was developed to utilise creep compressional rheology *via* dynamical mechanical analysis, DMA, in compression mode. The results from the compressional rheology can be compared to the oscillatory rheology to verify them. Both can be fitted to a viscoelastic solid model shown in Figure 4.13 using equation 4.1 for the creep compliance from the creep testing on the DMA and equation 4.2 for small-amplitude oscillations on the Bohlin rheometer (elastic modulus G' and the frequency ω are the required experimental parameters):

$$J = \frac{1}{G_0} - \left(\frac{1}{G_0} - \frac{1}{G'_\infty} \right) \exp\left(\frac{G_0 t}{G'_\infty \lambda} \right) \quad 4.1$$

$$\frac{G'}{G'_\infty} = \frac{G_0/G'_\infty + (\lambda\omega)^2}{1 + (\lambda\omega)^2} \quad 4.2$$

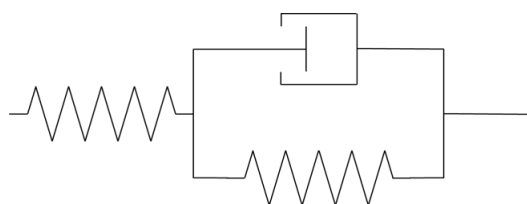


Figure 4.13: Viscoelastic solid model.³⁹

The prepared sample gels were tested in the DMA under a ramped compression force from 0 to 18 N. The results are shown in Table 4.3.

Table 4.3: Table showing DMA ramped compression force from 0 – 18 N results.

<i>n</i> -Alkane in dodecane		Compression μm	Observation
C₂₄	80 wt%	300	No observable dodecane expelled
	60 wt%	300	No observable dodecane expelled
	40 wt%	1380	Dodecane was expelled from the system at a force of roughly 10 N
	20 wt%	NA	Gel broken, and sample squashed at roughly 2 N
C₂₈	80 wt%	270	No observable dodecane expelled
	60 wt%	620	No observable dodecane expelled
	40 wt%	1400	Dodecane was expelled from the system at a force of roughly 9 N
	20 wt%	NA	Gel broken, and sample squashed at roughly 3 N

Increasing the wax wt% in the sample increases its strength as shown by the decrease in the total compression of the sample pellet after the DMA test, with the 20 wt% pellets not enduring the full compression force. Dodecane was expelled from the 40 wt% pellets of both wax samples. This can also be observed in the relaxation modulus (which can be thought of as the stiffness) of the sample, as shown in Figure 4.14.

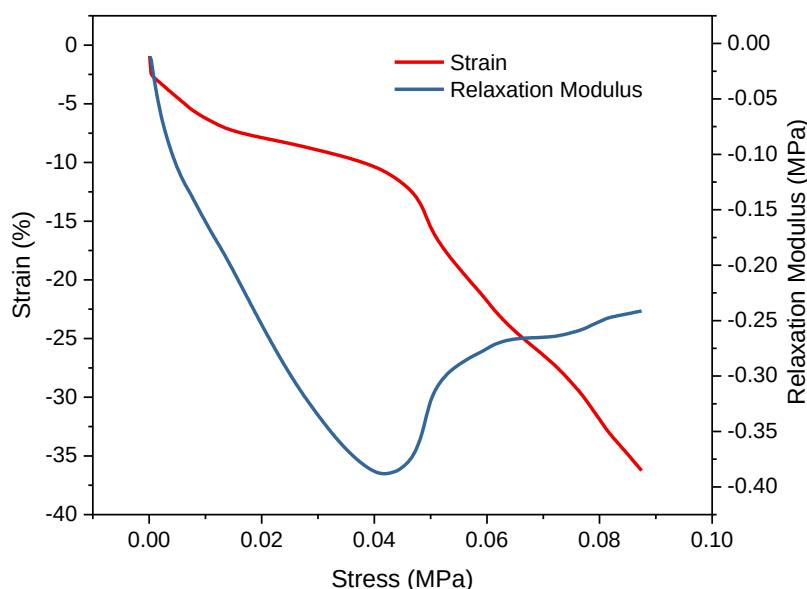


Figure 4.14: Graph of the response of 40 wt% single *n*-alkane C₂₈ sample showing a pronounced minimum in the relaxation modulus as the dodecane is expelled from the system.

From the ramp tests, 40 wt% and 60 wt% samples were selected for compressional stress testing as 20 wt% was considered too weak and 80 wt% too

strong. The stress and strain testing needed to be conducted in the linear viscoelastic region, before any significant deformation of the sample occurs. In Figure 4.14 this can be seen in the region of relatively flat strain from 0 to 0.04 MPa or 0 to 9 N.

However, 40 wt% C₂₄ was the only gel weak enough to test in the Bohlin rheometer. An amplitude sweep showed a very large viscoelastic region to the limits of the rheometer, so a frequency sweep was conducted at 2000 Pa. This fitted well to the model shown above giving $G_0 \sim 1 \times 10^6$ Pa. The results and fit are shown in Figure 4.15.

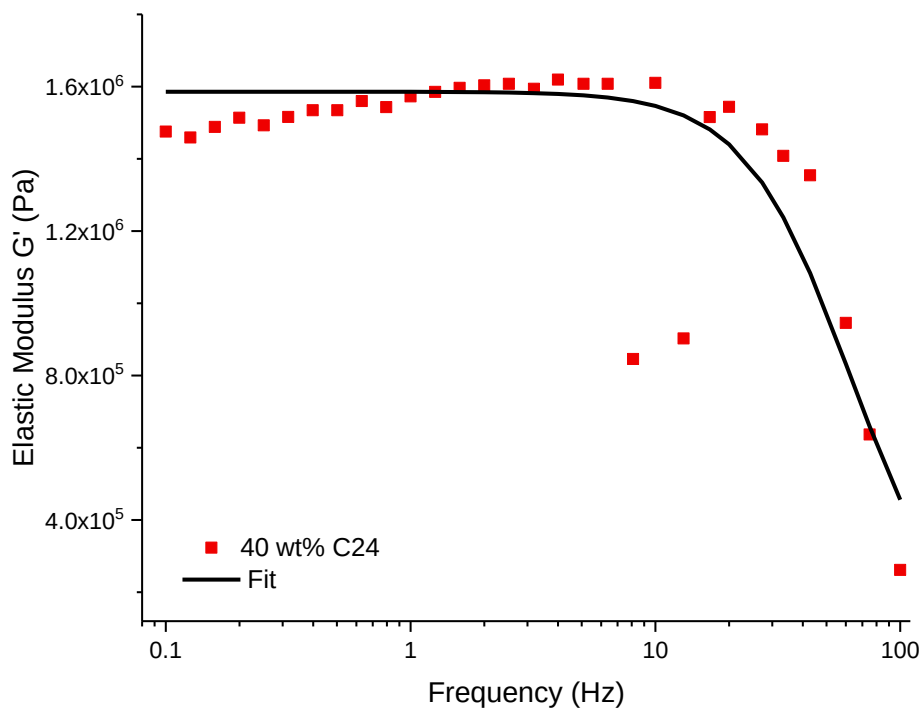


Figure 4.15: Oscillatory frequency sweep at 2000 Pa of C₂₄ 40 wt%. Fitted with viscoelastic solid model for small-amplitude oscillations.

Creep testing was conducted by applying an initial stress, σ , and the resulting strain response, $\varepsilon(t)$, was measured. This allows calculation of the creep compliance, $J = \varepsilon(t) / \sigma$. To ensure this is within the linear viscoelastic region of the gel, the relaxation modulus, $G = \sigma / \varepsilon$, for the system also needs to be calculated and a Laplace transform performed. G was found by compressing the sample at a force for 5 minutes then noting the strain at the end of the test. Next a strain test was conducted and the sample compressed to the noted strain and the stress response measured. Mathematica was used to calculate the Laplace transform of the samples, these gave the results within the same order of magnitude as $\bar{J}(s)\bar{G}(s) = 1$ within Laplace space.

The DMA compression experiments were conducted on 40 wt% C₂₄ at -4% and -6% strain, corresponding to roughly to 4N and 6N Pa of stress, to compress the bulk of the wax pellet. The Laplace transform of the J (strain controlled) and G (stress controlled) experiments gave a value close to 1, so we can be confident that we are working within the linear viscoelastic region.

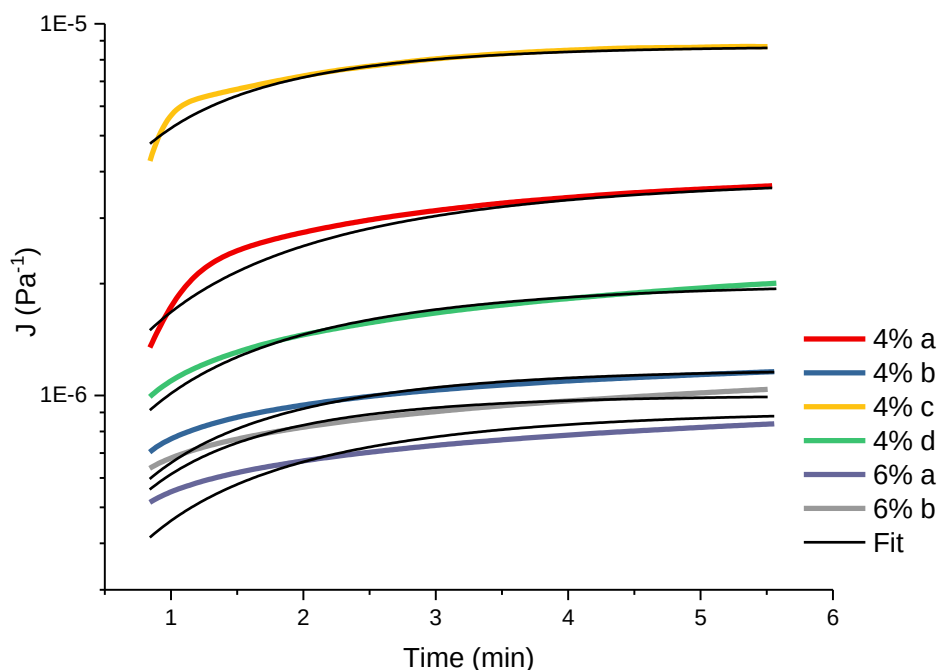


Figure 4.16: Creep compliance data from C₂₄ 40 wt% DMA fitted with viscoelastic solid model

The viscoelastic solid model shown above was fitted to the creep compliance data. The imperfect fits are shown in Figure 4.16. The fitting parameters from both the DMA and Bohlin data listed in Table 4.4.

Table 4.4: Fitting parameters of the viscoelastic model to DMA creep compliance data and Bohlin small-amplitude oscillations.

40 wt% C ₂₄	$G_0 \times 10^5$ (Pa)	$G'_\infty \times 10^6$ (Pa)	λ
DMA – 4% a	2.60	3.50	9.00
DMA – 4% b	8.50	8.00	9.00
DMA – 4% c	1.15	1.20	7.00
DMA – 4% d	5.00	5.00	10.00
DMA – 6% a	11.00	11.00	10.00
DMA – 6% b	10.00	9.00	8.00
Bohlin	15.86	0.015	0.016

The G_0 parameters between the repeated DMA data and Bohlin data are the same order of magnitude. This suggests that wax alignment is not an issue and oscillatory rheology is a good technique to study the wax gels.

Samples of 60 wt% C_{24} and C_{28} and 40 wt% C_{24} and C_{28} were also tested in the DMA at 2 N initial force which corresponds to roughly -2% strain. This was due to the 2 N data being much higher than the other creep responses so it was thought that there was a transition between 2 N and 4 N. Figure 4.17 shows the creep compliance of the 60 wt% C_{24} after compression by 2, 4, 6, 8 and 10 N initial force corresponding to 0.01, 0.02, 0.03, 0.04 and 0.05 Pa of initial stress. Similar results were found with 40 wt% and 60 wt% C_{24} and C_{28} .

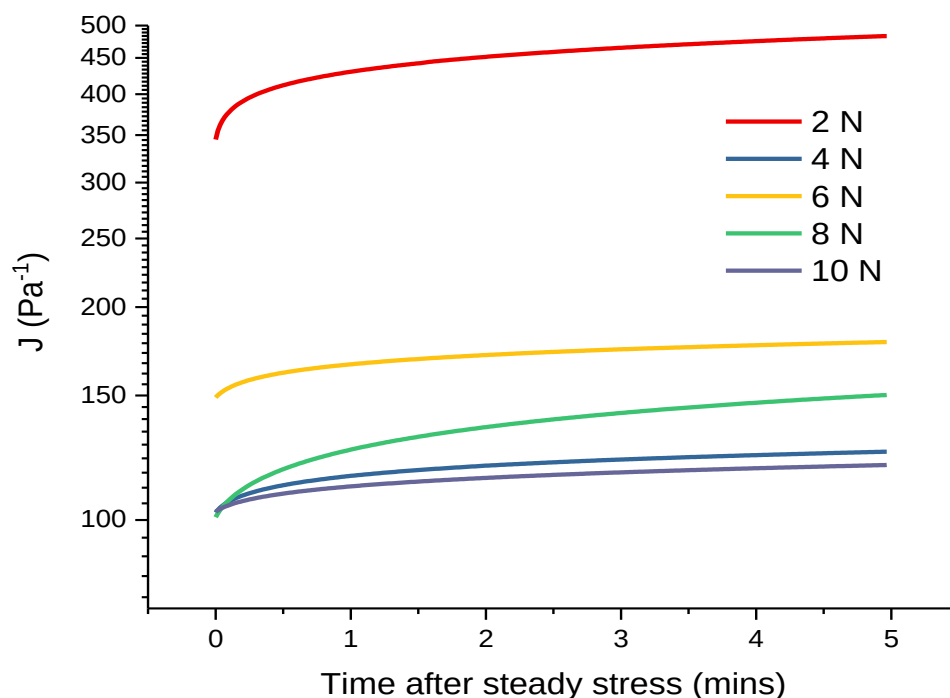


Figure 4.17: Creep compliance of 60 wt% C_{24} after compression by 2, 4, 6, 8 and 10 N initial force.

The Laplace transform was performed again confirming that 2 N is within the linear viscoelastic region for these model diesel gels. Figure 4.18 shows the viscoelastic solid model fitted to the creep compliance. This model fits the data quite well. The fitting parameters for the model are shown in Table 4.5.

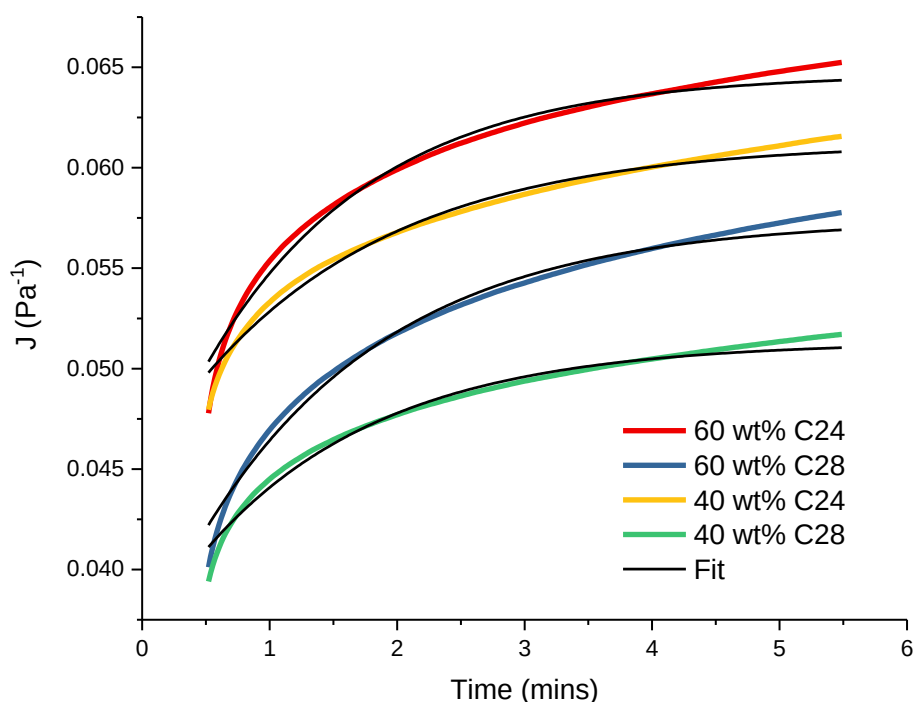


Figure 4.18: Creep compliance data from DMA fitted with viscoelastic solid model shown above.

Table 4.5: Fitting parameters of the viscoelastic model to DMA creep compliance data

	G_0 (Pa)	G'_∞ (Pa)	λ
60 wt% C₂₈	17.4	23.7	1.1
60 wt% C₂₄	15.5	19.9	1.0
40 wt% C₂₈	19.5	24.3	1.1
40 wt% C₂₄	16.3	20.1	1.3

The 2N data fitting from the DMA compression only gives $G_0 \sim 10$ Pa, whereas the Bohlin gives the $G_0 \sim 1 \times 10^6$ Pa. So, these creep and oscillation tests display a disparity of six orders of magnitude. We believe this is due to only compressing the sample by -2% strain so we may only be compressing the top section of the wax pellet. Whereas, there is good agreement between the creep and oscillatory tests when a higher strain is used and we are compressing the bulk of the sample. All the following rheological experiments were conducted on a Kinexus Lab+ rheometer.

4.2.2 Changing the amount of wax

4.2.2.1 Effect on the gel temperature

Samples were melted in an oven at 60 °C and then placed on the bottom plate at 60 or 40 °C then cooled to 10 °C at 2 °C min⁻¹ with a 1 mm gap. This cooling rate was considered slow enough to allow the crystals to grow slowly but fast enough to allow for acceptable test times. The gelation as the wax crystals grow was detected *via* single frequency oscillation measurements at 0.1 Hz and 0.1 % strain, which was low enough to not disturb the growing crystals. The volume fraction of wax in dodecane was increased from 0.15 to 0.4 and the experiment repeated.

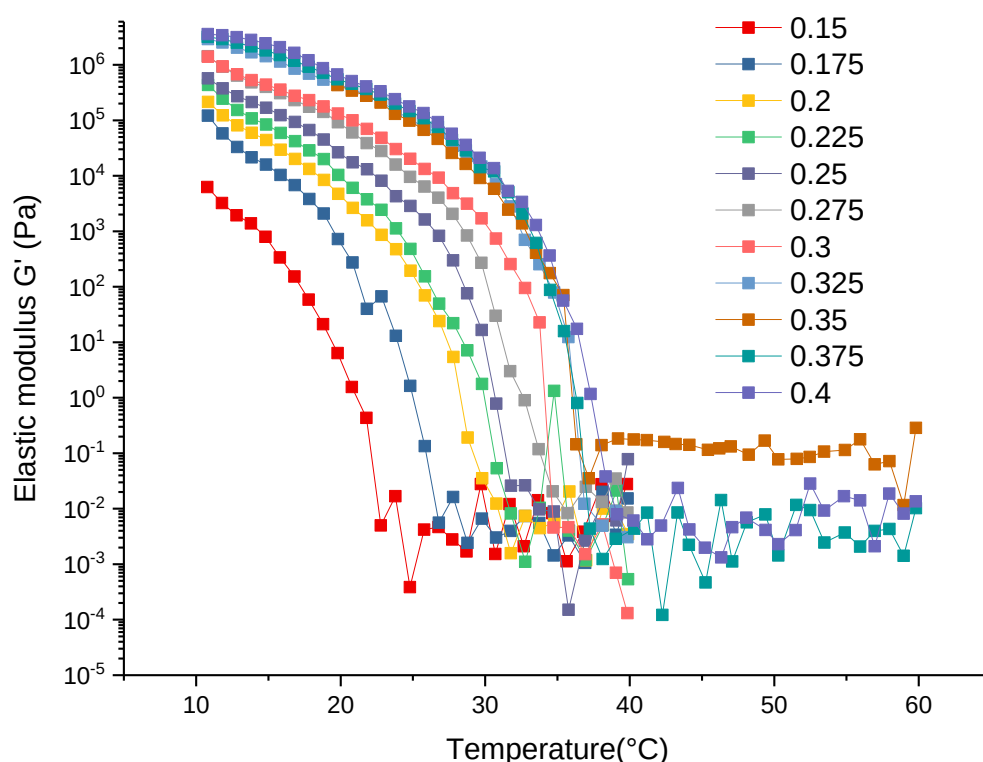


Figure 4.19: Oscillation single frequency over cooling at 2 °C min⁻¹ from 60 to 10 °C of volume fractions 0.15 to 0.4 of wax in dodecane.

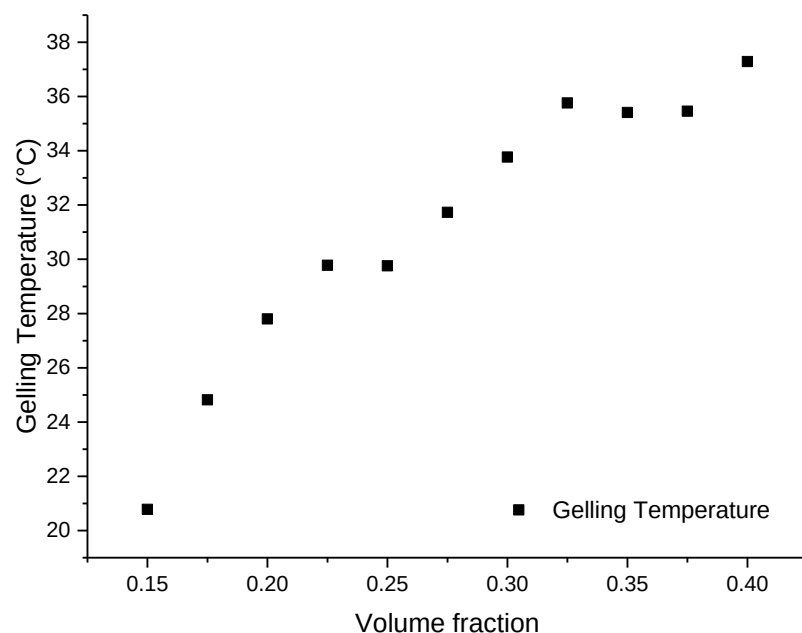


Figure 4.20: Gelling temperature of volume fractions 0.15 to 0.4 of wax in dodecane.

Figures 4.19 and 4.20 show that increasing the wax volume fraction from 0.15 to 0.4 increases the gelling temperature of the model diesel.

4.2.2.2 Effect on the strength of the gel

After the sample was cooled to 10 °C and held at 10 °C for 10 minutes, an oscillation frequency ramp from 0.05 to 15 Hz at 0.2% was conducted. To avoid delamination from the top plate the gap size was reduced to 0.9 mm.

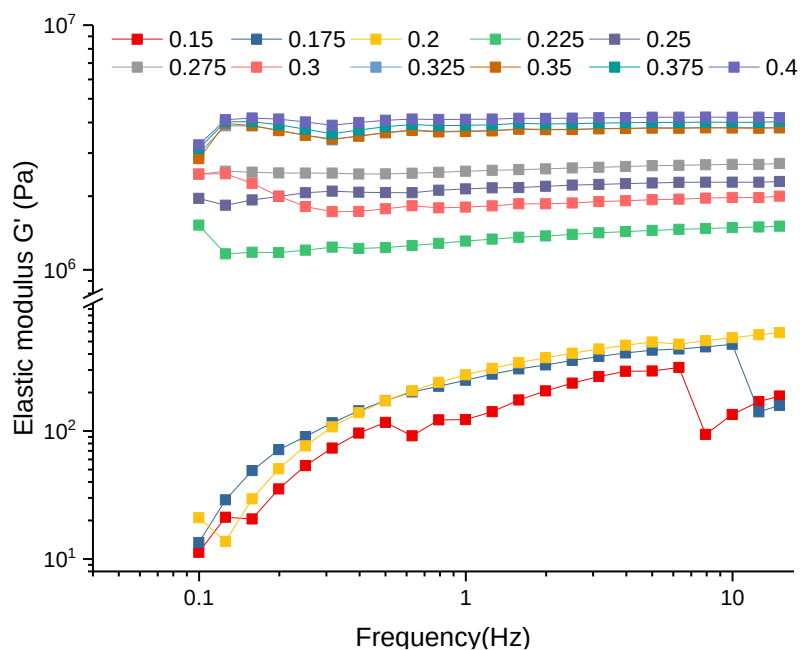


Figure 4.21: Frequency ramp from 0.05 to 15 Hz of volume fractions 0.15 to 0.4 of wax in dodecane.

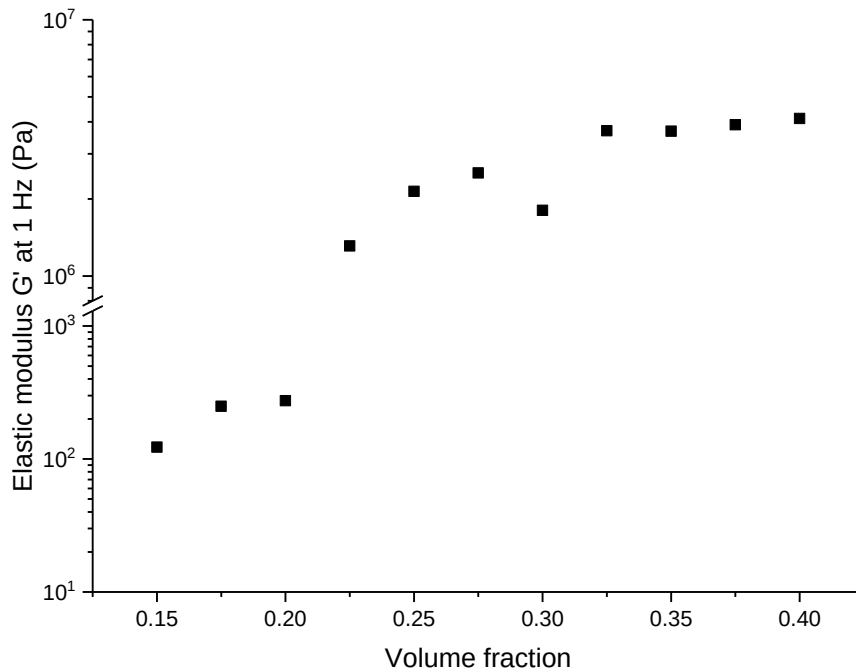


Figure 4.22: Elastic modulus at 1 Hz of volume fractions 0.15 to 0.4 of wax in dodecane.

Figures 4.21 and 4.22 show the increasing strength of the gel with increasing volume fraction 0.15 to 0.4. The largest increase of 10^6 Pa is seen between volume fractions of 0.2 and 0.225. Interestingly the break in the data between roughly $G' \sim 10^2$ or 10^6 Pa seems to coincide with the G_0 parameters calculated from the two sets of creep rheology data. This could suggest that the -2% compression creep test (which gave $G_0 \sim 10^2$ Pa) was only compressing the top section of the wax pellet which had a much lower volume fraction ($0.15 < \Phi_v < 0.2$) of the wax crystals than the bulk ($\Phi_v \sim 0.28$).

4.2.3 Changing the additives

The 10 wt% model diesel was doped with WASA, EVA, C_{22} FVA and the organic salt at different concentrations to explore the impact of these additives on the system.

4.2.3.1 Effect on the gel temperature

The concentration of additive was increased from 0 to 10 wt% and the test performed in the same way as section 4.2.2.1.

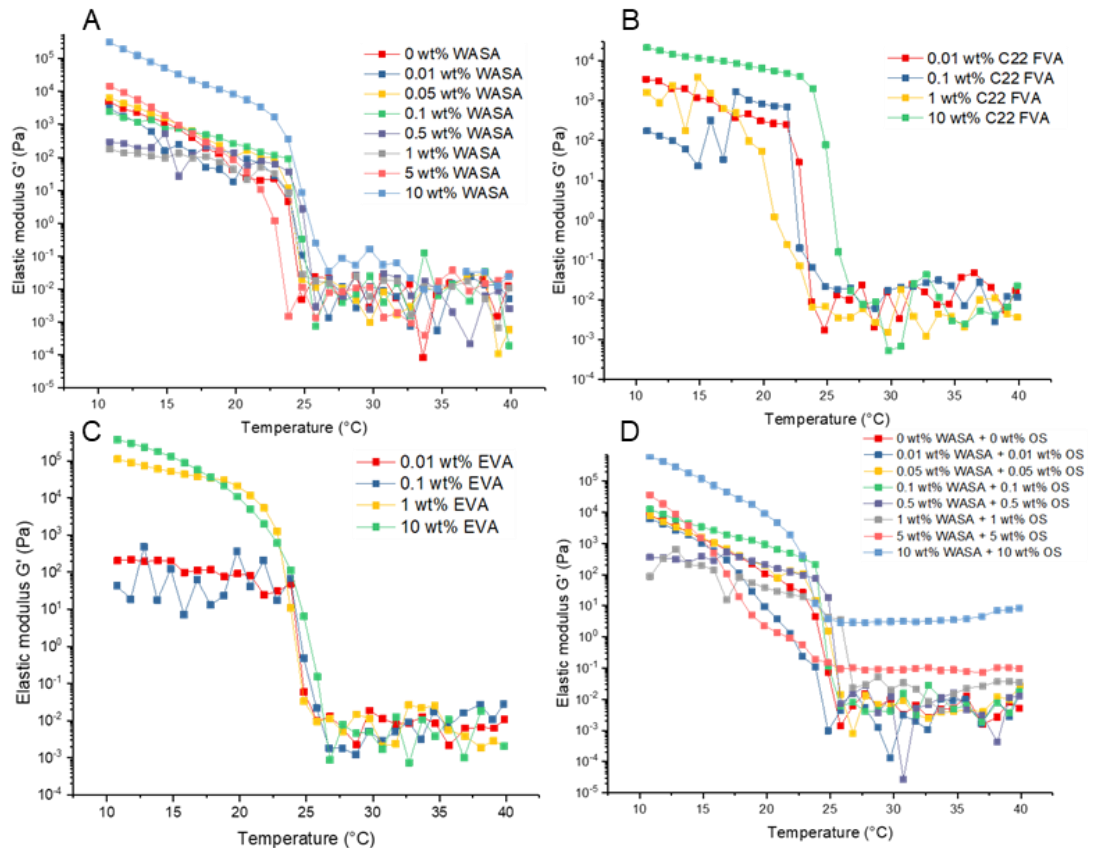


Figure 4.23: Oscillation single frequency over cooling at $2^{\circ}\text{C min}^{-1}$ from 40 to 10 $^{\circ}\text{C}$ of various wt% of WASA (top left), C₂₂ FVA (top right), EVA (bottom left) and WASA and organic salt (bottom right).

Figure 4.23 shows the elastic modulus as the sample was cooled of all the samples. Varying the amount of WASA (shown in Figure 4.23 A) did not significantly vary the gelling temperature of the model diesel. All samples gelled between 22 and 24 $^{\circ}\text{C}$.

Increasing the wt% of EVA (shown in Figure 4.23 C) also did not change the gelling temperature of the sample, with all samples gelling at roughly 24 $^{\circ}\text{C}$.

Conversely, increasing the amount of C₂₂ FVA (shown in Figure 4.23 B) reduced the gelling temperature from 23 $^{\circ}\text{C}$ at 0.01 wt% to 21 $^{\circ}\text{C}$ at 1 wt%. However, at 10 wt% the gelling temperature was increased to 25 $^{\circ}\text{C}$.

Organic salt was added in equal amounts to the WASA (WASA+OS) (shown in Figure 4.23 D) from 0 to 10 wt%. Varying the amount of WASA+OS did not significantly vary the gelling temperature of the model diesel. All samples began to gel between 22 and 24 $^{\circ}\text{C}$, similarly to the samples with WASA only.

4.2.3.2 Effect on the strength of the gel

The WASA, C₂₂ FVA, EVA and WASA+OS samples were tested for gel strength using an oscillation frequency ramp from 0.05 to 15 Hz at 0.2%. All the samples seen in section 4.2.3.1 were run after cooling and holding at 10 °C for 10 minutes. The frequency ramps for these samples are shown in Figure 4.24 with additive doping WASA, C₂₂ FVA, EVA and WASA+OS respectively.

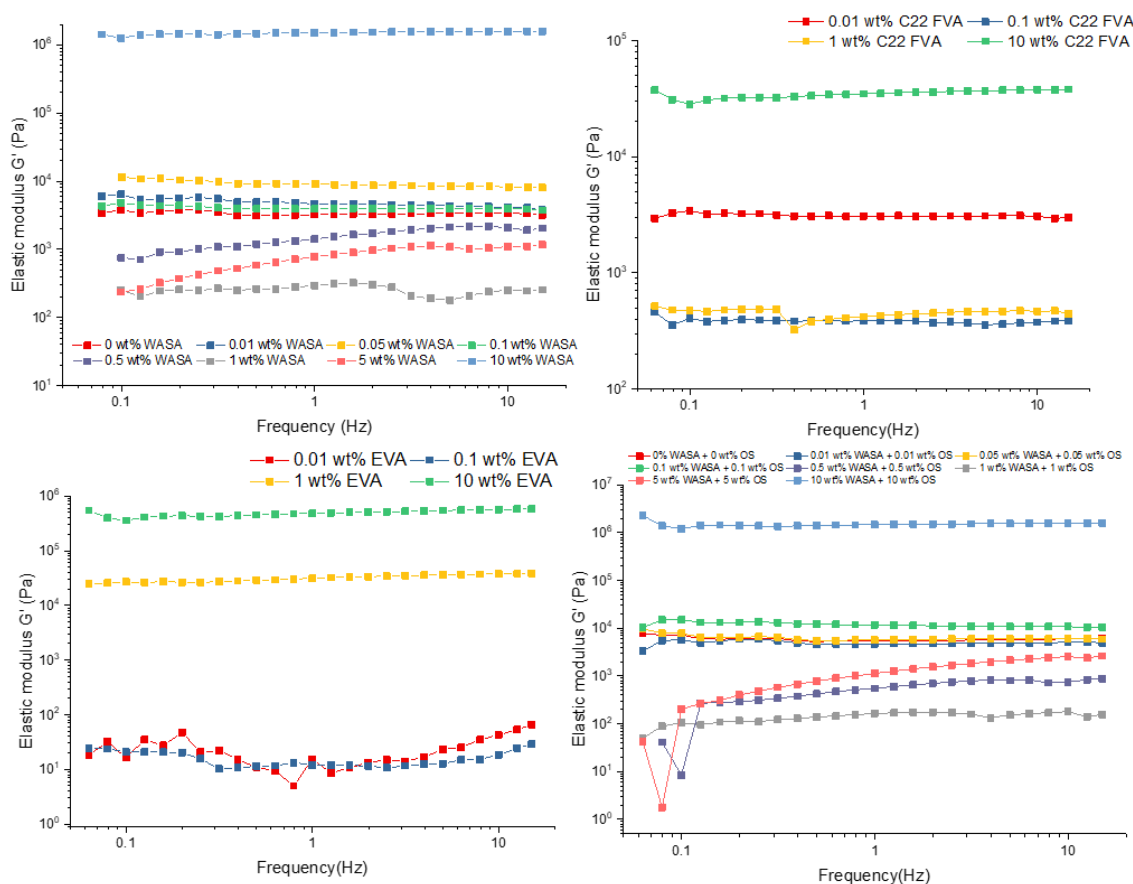


Figure 4.24: Frequency ramp from 0.05 to 15 Hz of model diesel doped with 0.01 to 10 wt% WASA (top left), C₂₂ FVA (top right), EVA (bottom left) and WASA and organic salt (bottom right).

The elastic moduli, G' , of some samples vary slightly over the frequency ramp, thus an average of the elastic modulus at 0.1, 1 and 10 Hz were taken and plotted against doped weight percent of the different additives, shown below in Figure 4.25.

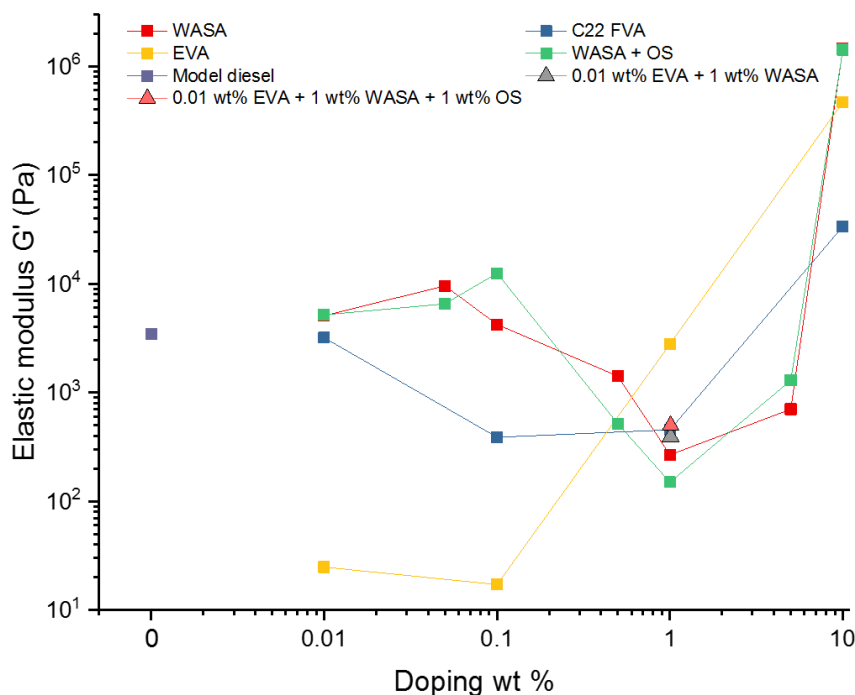


Figure 4.25: Averaged elastic modulus of doped samples vs the wt% of doping of WASA, C22 FVA, EVA, WASA and organic salt, EVA and WASA and EVA, WASA and organic salt.

The model diesel with 0 wt% doped additives had a G' of 3500 Pa. Adding WASA initially slightly increased the G' until 0.1 wt% WASA where G' decreased to a minimum of 270 Pa at 1 wt% WASA doping. At higher WASA doping G' increased and was dramatically increased at 10 wt%.

A similar trend was seen with C₂₂ FVA. At 0.01 wt% C₂₂ FVA the G' is similar to model diesel. Increasing the doping decreased G' to a minimum of 390 Pa at 0.1 wt% C₂₂ FVA. Then, similarly to WASA, at 10 wt% C₂₂ FVA G' dramatically increased.

When EVA was added to the model diesel at 0.01 and 0.1 wt% the gel was markedly weakened with a minimum in the G' of 17 Pa. Increasing the EVA doping significantly increased G' to a maximum of 0.5 MPa at 10 wt% EVA doping.

WASA and organic salt doped into the model diesel gave a similar result to that of WASA alone.

It is important to note that the additives alter the morphology and size of the wax crystals, as shown in chapter 3. In the un-doped model diesel sample the system gels due to the physical jamming of the larger wax crystals. As the additive doping

is increased the size of the wax crystals decreases thus breaking this jamming. This explains the decrease in the strength of the gel in the 0.01 to 1 wt% doping region of the additives. C₂₂ FVA and EVA decrease the size of the crystal more dramatically at smaller doping amounts than WASA. This explains why the G' of C₂₂ FVA and EVA doped systems are lower than that of WASA doped systems.

At 10 wt% doping the strength of the gel is dramatically increased across all additives. This could be due to the doubling of solid components in the dodecane as they contain 10 wt% wax and 10 wt% additive. It could also be due to a depletion interaction between the additive and wax crystals creating a gel.

At 1 wt% WASA the crystals have been reduced enough in size so that the physical jamming seen in the un-doped model diesel is no longer present. This implies that the gel is due to the presence of the WASA additive. The electrophoresis experiments show WASA imparting charge to the wax crystals suggesting that the gel could be electrostatic in nature. However, upon adding the organic salt, the strength of the gel is decreased only very slightly. If the gel was caused by electrostatics the organic salt should shield the wax crystals and significantly weaken the gel. This shows that the gel is not caused by simple electrostatics.

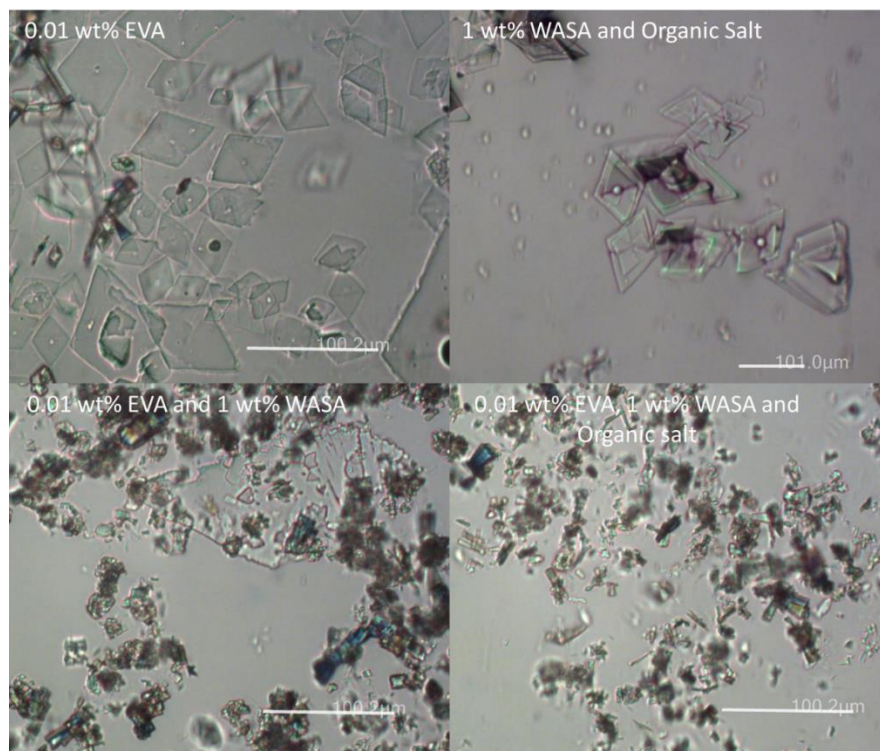


Figure 4.26: Microscopy pictures of rheology samples of 0.01 wt% EVA, 1 wt% WASA and organic salt, 0.01 wt% EVA and 1 wt% WASA and 0.01 wt% EVA, 1 wt% WASA and organic salt. White scale bar shows 100 μm

We wanted to eliminate the aspect of gelling caused by the morphology of the wax crystals and solely study the gelling due to the WASA. Thus, 0.01 wt% EVA was added to the samples with 1 wt% WASA and 1 wt% WASA and 1 wt% organic salt. 0.01 wt% EVA was chosen due to its large effect on the crystal morphology and large G' decrease. Again, these samples were tested (using an oscillation frequency ramp from 0.05 to 15 Hz at 0.2%) and an average of G' taken. Figure 4.25 shows that G' of the 0.01 wt% EVA + 1 wt% WASA and 0.01 wt% EVA + 1 wt% WASA + 1 wt% organic salt are very similar to that of the 1 wt% WASA. This suggests that the gelation is due to the WASA rather than the crystal morphology. Optical microscopy photos of the samples are shown in Figure 4.26 and show the small crystal size.

4.3 Settling testing

Some limited settling testing of the model diesel was conducted on multi-additive systems that resembled full industrial formulations. Time lapse photography allows the detection of the wax front as it settles over time (shown in Figure 4.27). The use of a MatLab script allows the images to be analysed and the wax front tracked. Settling testing development was conducted upon model diesel samples detailed in Table 4.6.

Table 4.6: 10 wt% model mixtures doped with EVA, FVA and WASA

#	EVA (wt%)	WASA (wt%)	C _{14/16} FVA (wt%)	C ₂₂ FVA (wt%)	25 °C appearance
1	0.03	0.12			Fine crystal suspension
2		0.03	0.12		Weak gel
3		0.03		0.12	Weak gel
4	0.06	0.24			Fine crystal suspension
5		0.06	0.24		Weak gel
6		0.06		0.24	Fine crystal suspension

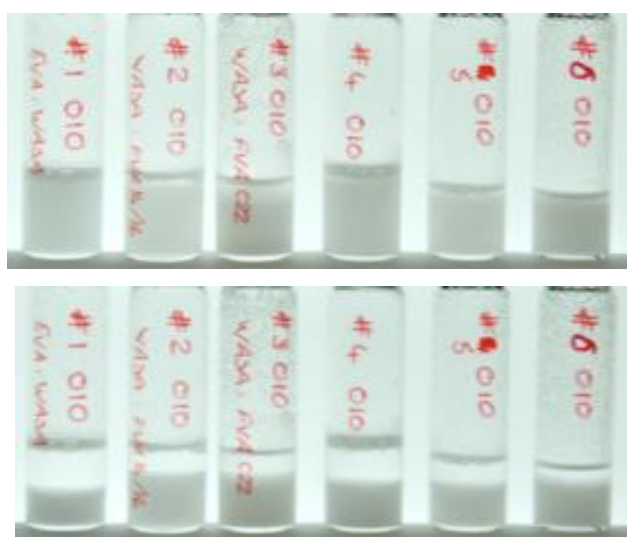


Figure 4.27: Time lapse photographs of wax settling. The top photos were taken immediately after mixing and the bottom after 2 hours.

Two different MatLab scripts were used: one written with help from Peter Dudfield and the other written by Dr Finn Box of the BPI Fluid Dynamics group. The results obtained were similar. The crystals were fully dispersed by stirring with a vortex mixer for 10 seconds before the test began.

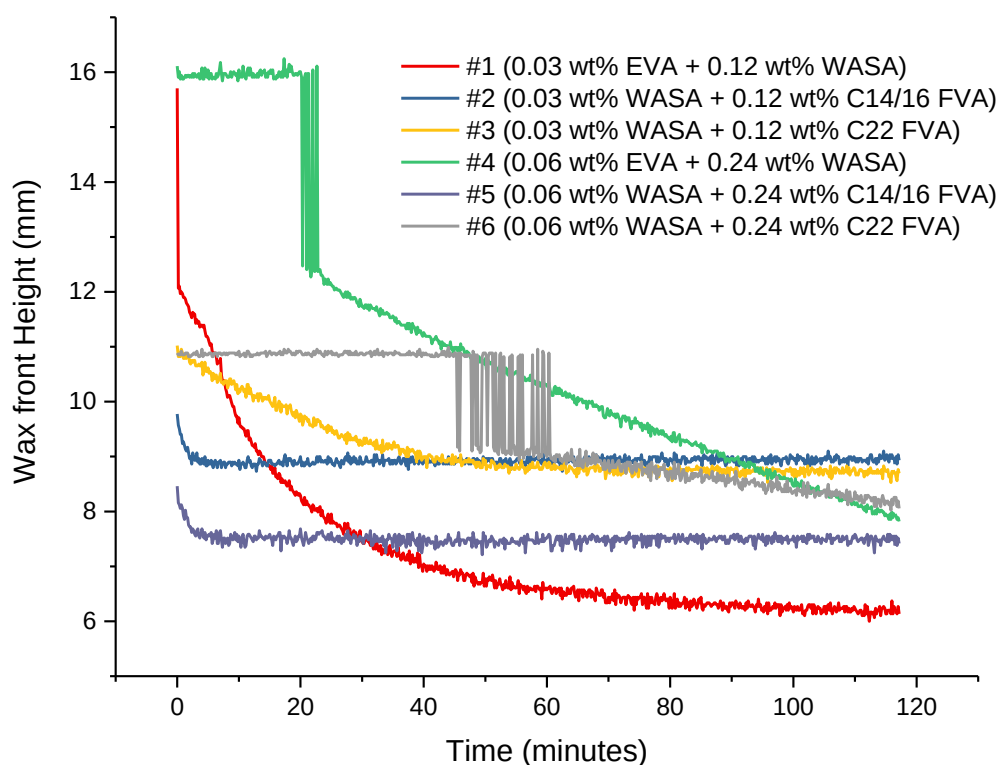


Figure 4.28: Graph showing the settling of samples as analysed by the first MatLab script.

Figure 4.28 shows the settling of the wax front as detected by the first MatLab script. A manual threshold between wax and solvent was set and the wax front was tracked down a single column of pixels. The sudden jump in samples 4 and 6 indicate that the script is struggling to distinguish the wax front. This might suggest that the latency time, seen as a plateau before the large drop, might also be an artefact of the MatLab script rather than a gelled stage followed by gel collapse.

The second script averaged the location of the wax front over several selected pixel columns, to try to eliminate these artefacts. The thresholding limit was automatically selected as the maximum within the area selected.

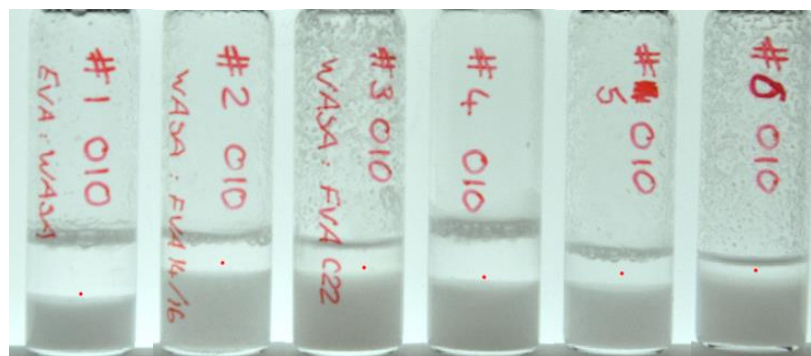


Figure 4.29: Settling samples using the second MatLab script. • - indicates where the MatLab script detects the wax front.

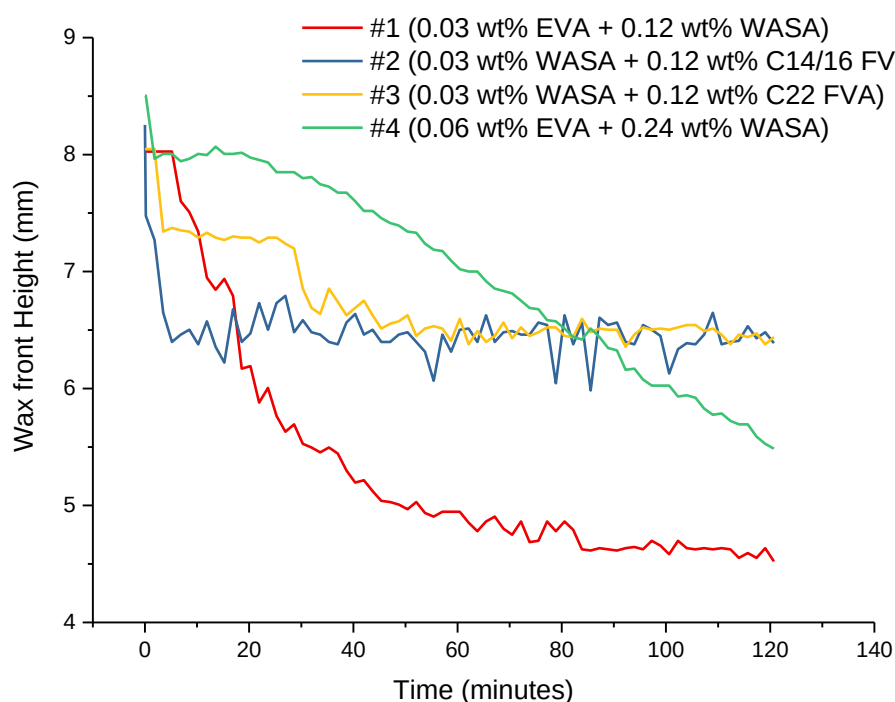


Figure 4.30: Graph showing the settling of experiment 010 samples as analysed by the second MatLab script.

Figure 4.29 shows that the second MatLab script does not always correctly detect the wax front particularly in samples 5 and 6 so these were omitted from Figure 4.30. For samples 1 to 4 the second MatLab script detects the wax front better than the first. The settling profiles appear to show a fast-initial settling velocity followed by a slower secondary settling. The wax crystal sizes were viewed *via* optical microscopy shown in Figure 4.31.

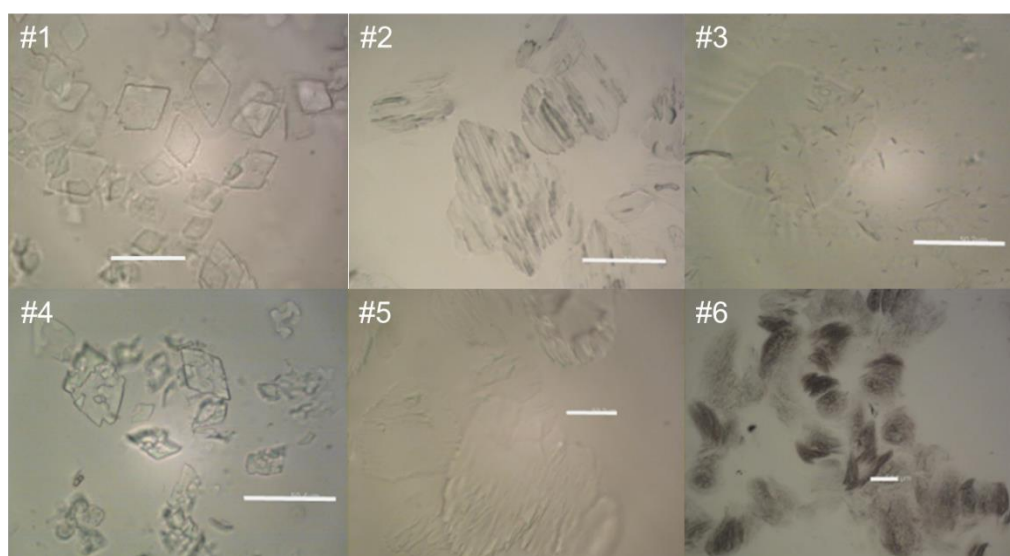


Figure 4.31: Wax crystal photo microscopy pictures of #1 – 6 doped samples. The white scale bar in each image indicates 50 μm .

The measured settling velocities were compared to predicted settling velocities as calculated by Stokes' law from the wax crystal sizes shown in Table 4.7 and Figure 4.32.

Table 4.7: Settling velocity from settling profiles as compared to calculated Stokes' velocity

	Rough crystal size (μm)	Stokes settling velocity (ms^{-1})	Initial settling velocity (ms^{-1})	Secondary settling velocity (ms^{-1})
1	50	5.67E-05	1.30E-03	1.00E-04
2	100	2.27E-04	5.10E-03	1.00E-05
3	10	2.27E-06	5.00E-04	4.00E-05
4	20	9.07E-06	5.10E-03	4.00E-04

The initial settling velocity, from the settling profiles, is an order of magnitude larger than the later settling velocities. For samples 1, 3 and 4 the secondary settling velocity is also faster than the calculated Stokes velocity. Whereas, for sample 2 the secondary settling velocity is slower than the calculated Stokes velocity.

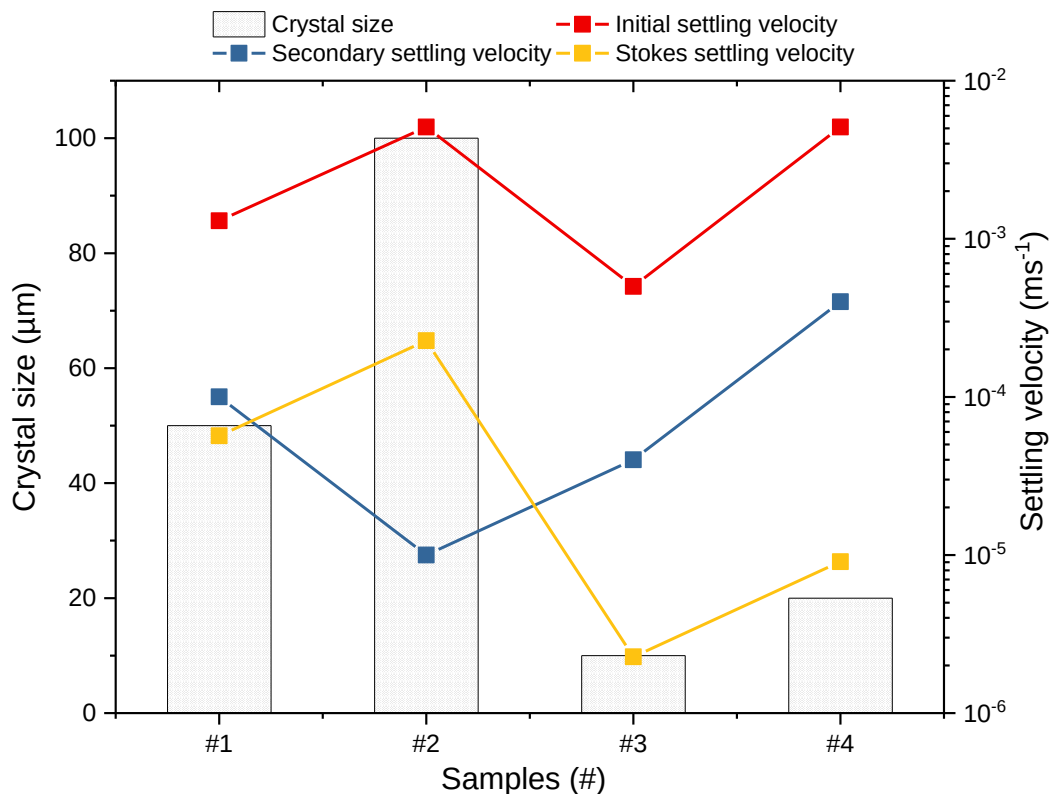


Figure 4.32: Graph showing comparison between various settling velocities and wax crystal size.

5 Results – Structure of WASA

The previous chapters discussed the effect of WASA on the model diesel, its location in the wax crystals and discussed how the anti-settling effect could occur. This chapter deals with trying to determine the structure of WASA in dodecane and the model diesel. This was done using small angle neutron scattering at the large scale facilities NIST in Washington and ISIS in Oxford.

5.1 SANS samples

5.1.1 Additive solubility

The solubility of WASA in dodecane was tested through various methods. Samples of 10 to 90 g additive per 100 g of dodecane were slowly heated at $0.5\text{ }^{\circ}\text{C min}^{-1}$ in a water bath and a temperature controlled sonicator. The temperature at which the WASA dissolved was noted. These samples were also run in a Crystal 16 turbidity sensor. In the Crystal 16 the samples were; heated to $60\text{ }^{\circ}\text{C}$, held at $60\text{ }^{\circ}\text{C}$ for an hour, cooled to $10\text{ }^{\circ}\text{C}$ at $2^{\circ}\text{C min}^{-1}$, held at $10\text{ }^{\circ}\text{C}$ for 5 mins and then heated at $2^{\circ}\text{C min}^{-1}$ to $60\text{ }^{\circ}\text{C}$. This cycle was repeated twice. The 100% clear turbidity was set at $60\text{ }^{\circ}\text{C}$ when the WASA was fully dissolved for all samples. The temperature at which the sample drops below 100% transmittance during cooling is called the cloud point indicating the WASA precipitating from the dodecane. Post precipitation, during the heating ramp of the cycle, the temperature at which 100% transmittance is regained is called the clear point as shown in Figure 5.1.

The clear point from the Crystal 16 and the dissolution temperatures from the water bath and sonicator methods were compared in Figure 5.2. The Crystal 16 gave clear points several degrees below the other methods. This could be due to the higher sensitivity of the turbidimeter or due to the sample being stirred.

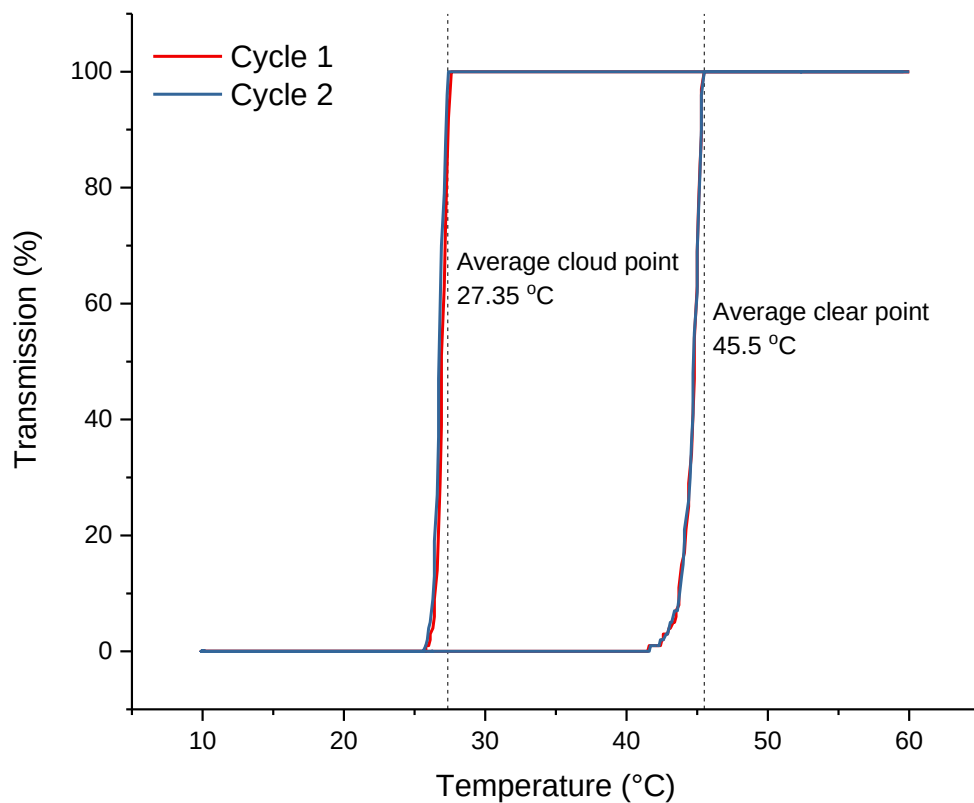


Figure 5.1: Example data from Crystal 16 showing cloud point and clear point of 30 g of WASA per 100 g dodecane.

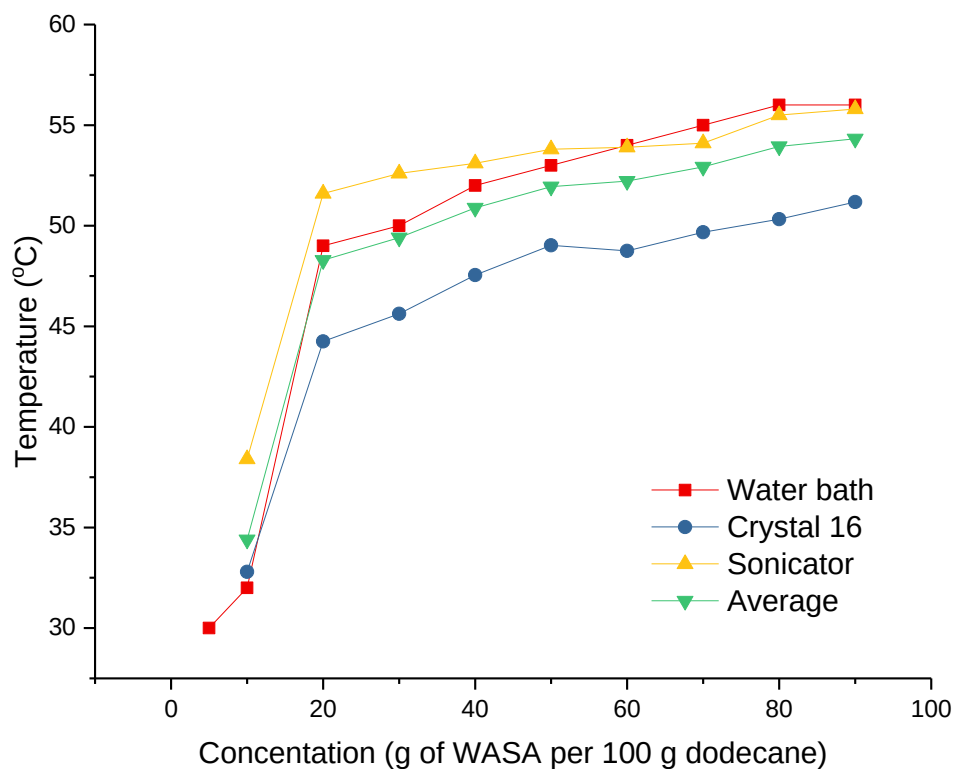


Figure 5.2: Clear points for WASA in dodecane from water bath, sonicator and Crystal 16 methods.

The Crystal 16 experiments were repeated for C₂₂ FVA. The cloud and clear points for WASA and C₂₂ FVA are shown in Figure 5.3.

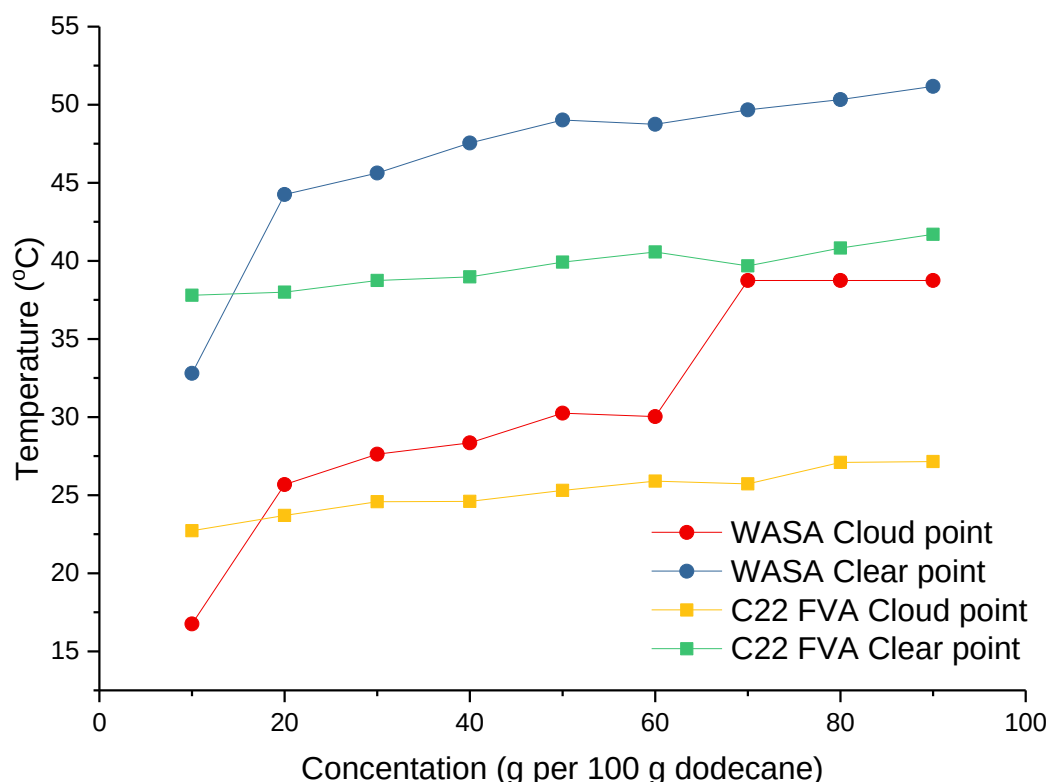


Figure 5.3: Cloud and clear points of various concentrations of WASA and C₂₂ FVA measured on a Crystal 16.

The solubility of WASA in dodecane is more concentration dependent and generally less soluble than C₂₂ FVA. WASA precipitates at an average temperature of 28 ± 5 °C over the concentration range. Whereas, C₂₂ FVA precipitates at an average temperature of 25 ± 2 °C over the range of concentrations tested. These experiments give us a precipitation temperature range of various concentrations of WASA and C₂₂ FVA.

5.1.2 Differential scanning calorimetry temperature profiles

Due to not knowing what concentration of WASA or C₂₂ FVA would be required in the neutron beamline to get enough scattering intensity the thermal profile of multiple WASA and C₂₂ FVA concentrations in the model diesel were tested. The WASA DSC profile was conducted at 2 °C min⁻¹ and the C₂₂ FVA at 10 °C min⁻¹ shown in Figure 5.4.

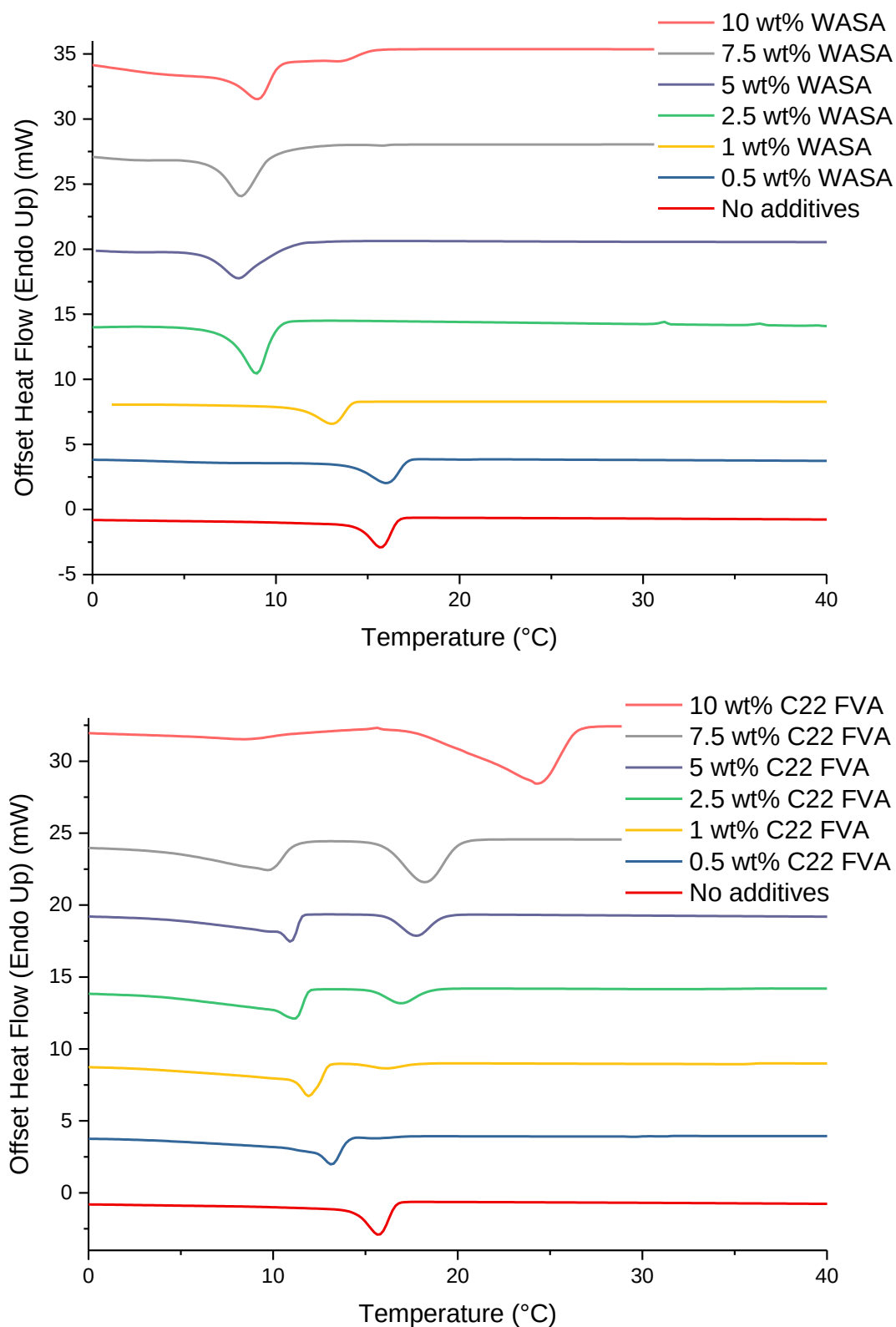


Figure 5.4: DSC traces of 10 wt% model diesel with various wt% WASA (top) and C₂₂ FVA (bottom).

From this data and the solubility data the sensible temperature ranges for various concentrations of WASA and C₂₂ FVA can be determined. For the lower wt% concentrations (< 2.5 wt%) of the additives; 40 °C should give the scatter of

dissolved additives with and without dissolved wax, 30 °C should give the scatter of partially dissolved additives with and without dissolved wax, 25 °C should give the scatter of the additives with and without dissolved wax and 15 and 20 °C should give the scatter of the additives with and without wax. Lower temperatures were not used due to the risk of condensation forming on the glass SANS cells.

The concentration used for the NIST beam run to obtain sufficient scattering intensity was 2.5 wt% WASA while at ISIS we were able to use much lower concentrations as low as 0.05 wt% WASA.

5.1.3 Deuterated WASA and contrast

Neutron contrast is provided *via* deuteration. This is required to be able to highlight the different aspects of the samples. Deuterated dodecane and *n*-alkanes were purchased as described in section 2.1.4. Two variations of deuterated WASA were made as detailed in section 2.1.4.1. The fully deuterated WASA has deuterated aromatic and aliphatic components (D-WASA) whereas the partially deuterated WASA only has deuterated aromatic components (Dp-WASA). Once 2.5 wt% D and Dp-WASA were doped into the model diesel samples, we noticed that the deuterated versions of the WASA were a lot less soluble than the H-version. Neither dissolved in the D or H-dodecane model diesel at 40 °C whereas the H-WASA was fully dissolved. The D and Dp-WASA samples finally dissolved at 80 °C. However, when left to recrystallise they did not give fine wax crystals, as observed for H-WASA. Thus, the deuterated WASAs were not used for contrast on the neutron beam runs. The contrasts used are detailed in Figure 5.5.

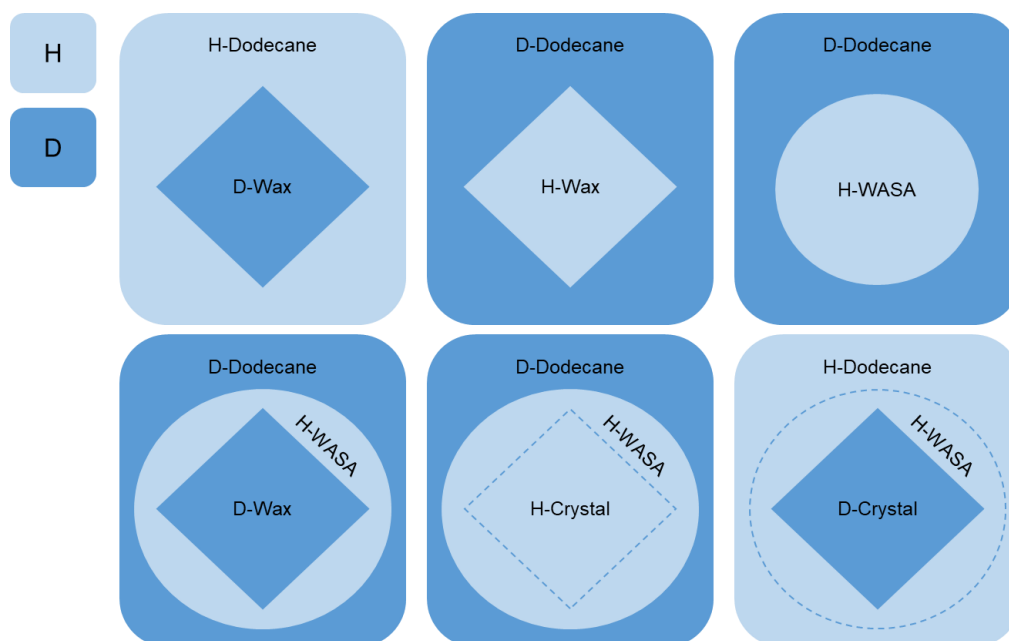


Figure 5.5: Contrasts used in neutron beam line experiments.

After the beam line experiments, the unused D and Dp-WASA doped samples were run in a DSC with the results shown in Figure 5.6. This shows that upon addition of either of the deuterated WASA versions the crystallisation temperature, T_c , of the model diesel is not reduced. The model diesel without any additives has a T_c of 18 °C. Upon addition of 2.5 wt% H-WASA the T_c is reduced to 14 °C. However, upon addition of 2.5 wt% of the D-WASA or Dp-WASA the T_c remains high at 19 °C. There are also crystallisation peaks at 38 °C and 40 °C in the D-WASA and Dp-WASA respectively. Similar results were found for all deuterated and non-deuterated combinations of wax and dodecane.

This suggests that the deuterated versions of the WASA do not affect the model diesel and do not crystallise with the wax crystal as seen with H-WASA. The peaks around 39 °C also suggest that the deuterated WASA versions precipitate from solution before the wax crystallises. This explains why the deuterated WASA versions do not affect the T_c of the model diesel or dramatically alter appearance of the wax or sample.

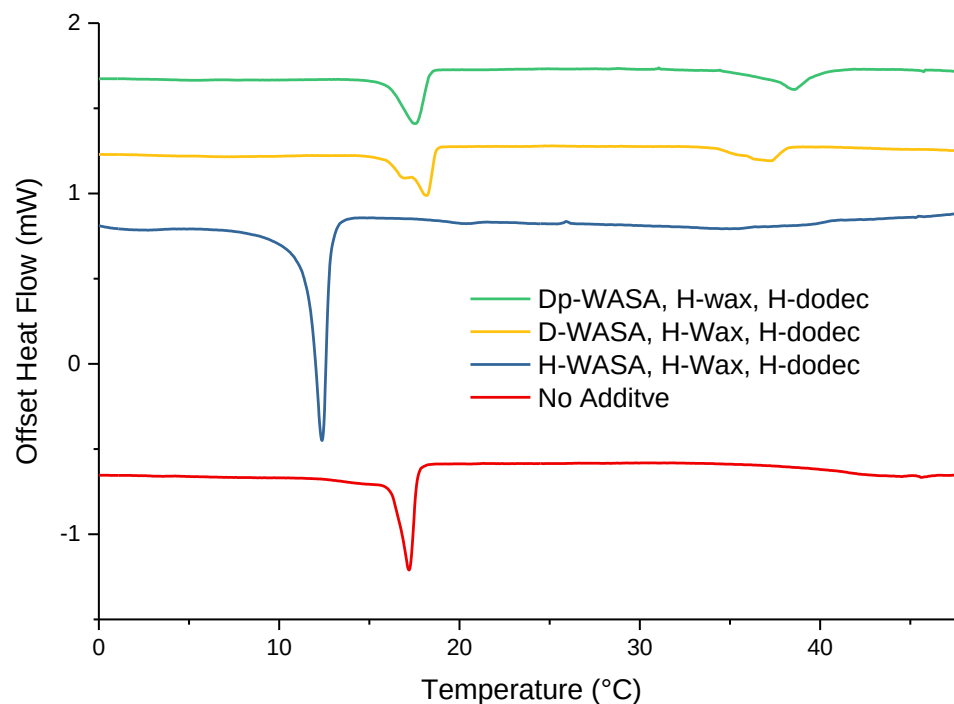


Figure 5.6: DSC traces of 10 wt% model diesel with; no additives, 2.5 wt% H-WASA, 2.5 wt% fully D-WASA and 2.5 wt% partially D-WASA (Dp-WASA).

Optical microscopy of the 2.5 wt% fully deuterated WASA sample shows two different types of species as shown in Figure 5.7. The wax crystals appear rhombic and are over 100 μm in size, whereas with 1 wt% H-WASA the wax crystals are $\sim 16 \mu\text{m}$ in size. The dark needle-like crystal is strongly suspected to be due to the D-WASA.

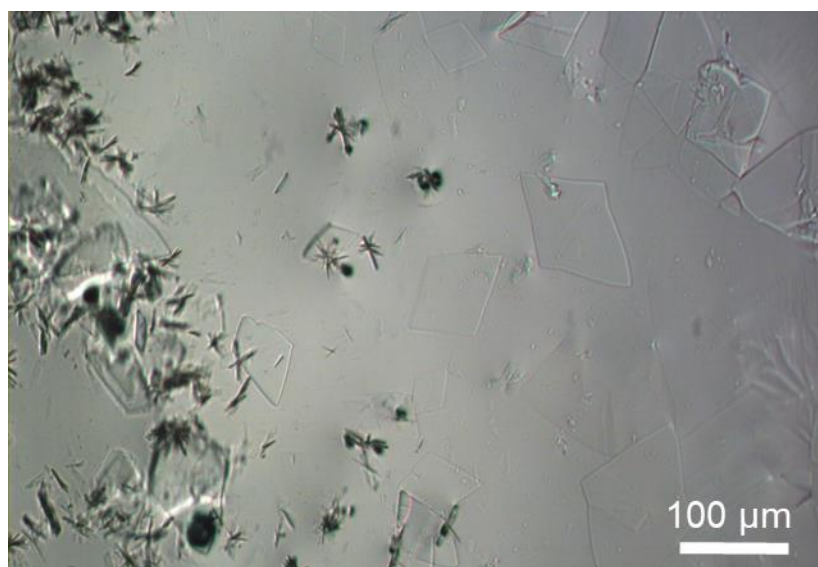


Figure 5.7: Optical microscopy image of 2.5 wt% fully deuterated WASA in model diesel.

5.2 NG7 SANS NIST

The NG7 SANS beamline gave a Q range from 2.02×10^{-4} to $1.198 \times 10^{-1} \text{ \AA}^{-1}$ from a detector at 4 m and 13 m. The samples ran in NG7 at NIST are listed in Table 5.1 along with background samples of D and H-dodecane. Samples were run in banjo shaped cells. D-dodecane samples had a 5 mm path length and H-dodecane samples had a 1 mm path length. Hydrogen gives lots of incoherent background scattering so it is advantageous to minimize the amount of hydrogen in a sample and reduce the path length of hydrogen solvent samples to give the best signal. All samples were prepared as previously described, kept in a 60 °C oven and hot pipetted into warmed banjo cells.

Data were reduced using Igor software from the neutron beam facility and then fitted using SasView software. The scattering length densities (SLD) inputted into the fitting software, were calculated according to the average atomic scattering length of the material atoms and their number density. During fitting SLDs were allowed to float a little to allow for potential contamination of the sample. SLDs are shown in Table 5.2.

Table 5.1: Sample list run on NG7 SANS beam run

Sample	Additive wt%	Temperature (°C)
H-WASA in D-dodecane	2.5	30
		25
		20
		15
10 wt% H-wax in D-dodecane	0	30
		25
		20
		15
10 wt% D-wax in H-dodecane	0	30
		25
		20
		15
H-WASA, H-wax in D-dodecane	2.5	30
		25
		20
		15
H-WASA, D-wax in D-dodecane	2.5	30
		25
		20
		15
H-WASA, D-wax in H-dodecane	2.5	30
		25
		20
		15

Table 5.2: Scattering Length Densities of materials used in SANS samples.

Component	H-contrast ($\text{\AA}^{-2}$)	D-contrast ($\text{\AA}^{-2}$)
Wax*	-3.86E-07	6.11E-06
Dodecane	-4.63E-07	6.43E-06
WASA	-1.20E-07	
C₂₂ FVA**	8.04E-08	
* Wax SLD is averaged over C ₂₀ , C ₂₄ , C ₂₈ and C ₃₂ alkanes.		
** Calculated from the monomer		

5.2.1 Wax in dodecane

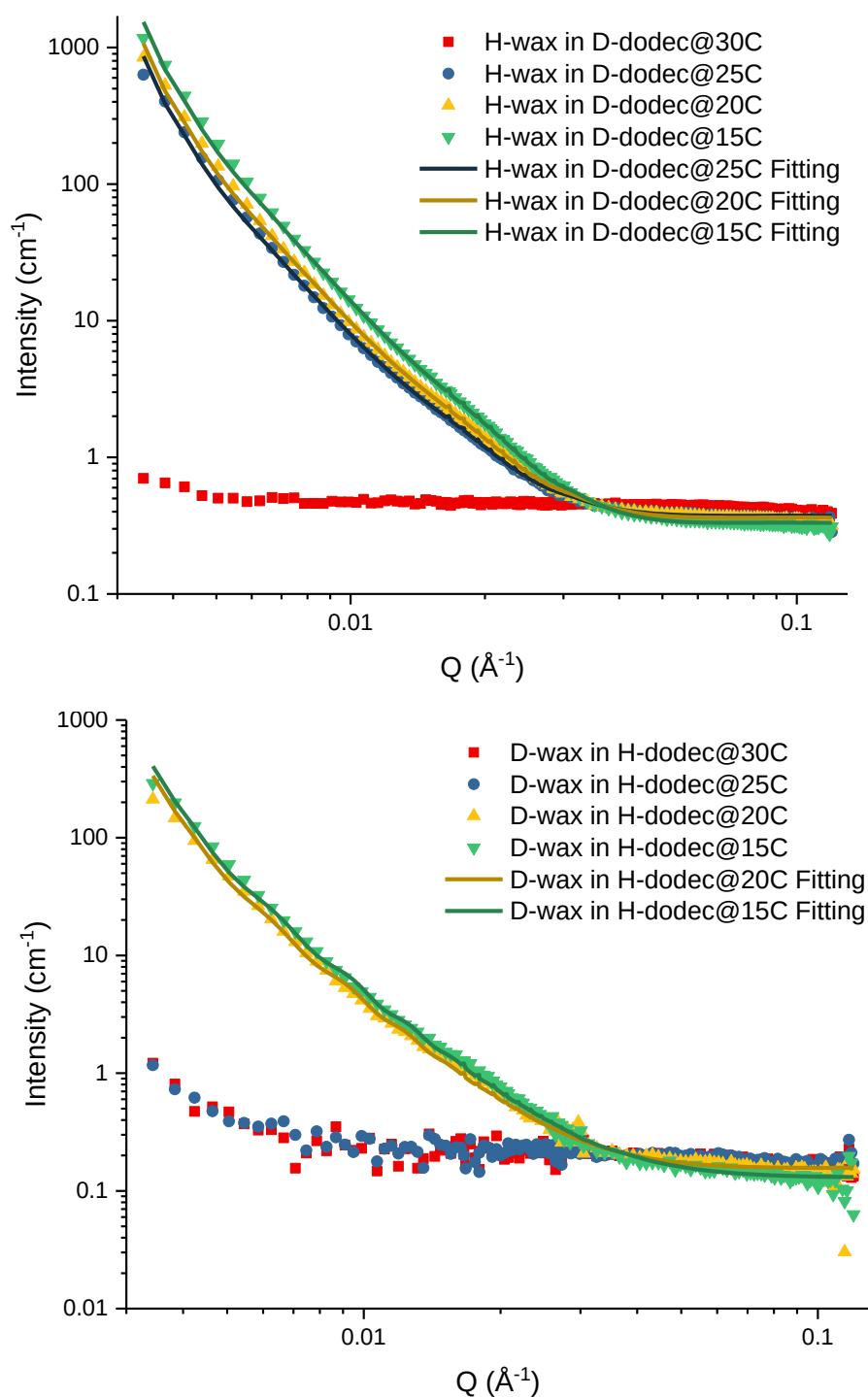


Figure 5.8: SANS data for samples of H-wax in D-dodecane (top) and D-wax in H-dodecane (bottom) at 30, 25, 20 and 15 °C and fitting to cylinder model.

Figure 5.8 shows the SANS data of the 10 wt% wax in dodecane samples at different temperatures in the two different contrasts. H-wax in D-dodecane at 30 °C and D-wax in H-dodecane at 30 and 25 °C showed very little intensity due to the wax being dissolved, so these were not fitted. The lower temperatures gave a higher intensity as the wax crystallised. All samples were fitted with the Guinier-

Porod function, which calculates the scattering for a generalized Guinier/power law object. It is an empirical model that can be used to determine the size and dimensionality of scattering objects. The Porod exponent obtained from this fit gives an initial indication of the form of the sample. An exponent or gradient of ~ 4 indicates that the structure is too large to be resolved by the neutrons and the scattering is from the surface of the structure. Table 5.3 shows the Porod exponent for the wax samples at low Q .

Table 5.3: Porod exponent from Guinier Porod function of wax SANS samples at various temperatures.

Sample	Porod exponent from Guinier Porod
H-wax in D-dodecane @ 30°C	0.9
H-wax in D-dodecane @ 25°C	4.1
H wax in D-dodecane @ 20°C	4.1
H-wax in D-dodecane @ 15°C	4.1
D-wax H-dodecane @ 30°C	0.9
D-wax in H-dodecane @ 25°C	0.9
D-wax in H-dodecane @ 20°C	4.0
D-wax in H-dodecane @ 15°C	4.1

The SANS data show a change in gradient at $\sim 0.03 \text{ \AA}^{-1}$ suggesting a length scale of 30 $\text{\AA}$ for a unit cell.

The samples were fitted to a cylinder model as this is the shape that the wax crystals most closely resemble, with a very small length and a large diameter, resembling a plate shown in Figure 5.9. The length and diameter parameters used in fitting are shown in Table 5.4 and the fits are shown in Figure 5.8. These sizes roughly agree with those seen from optical microscopy.

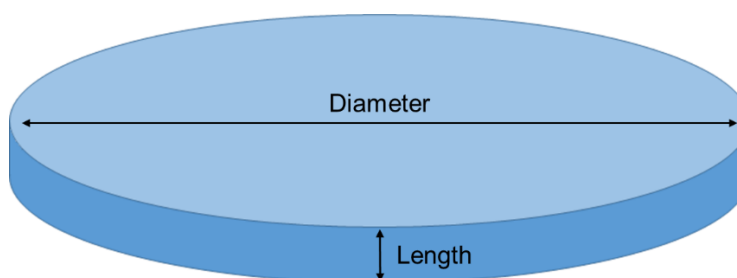


Figure 5.9: Diagram of cylinder showing diameter and length

Table 5.4: Parameters used for fitting wax SANS samples to cylinder model.

Sample	Length (Å)	Diameter (μm)
H-wax in D-dodecane @ 25°C	87	782
H wax in D-dodecane @ 20°C	87	782
H-wax in D-dodecane @ 15°C	91	780
D-wax in H-dodecane @ 20°C	53	502
D-wax in H-dodecane @ 15°C	33	492

This cylinder length could give the thickness of the wax crystal or the crystal unit cell. ~ 70 Å seems too thin for the wax crystals as they can be seen under the microscope so it is more likely a length scale due to the crystal unit cell, and the microscope is observing stacks of these cells.

5.2.2 2.5 wt% WASA in dodecane

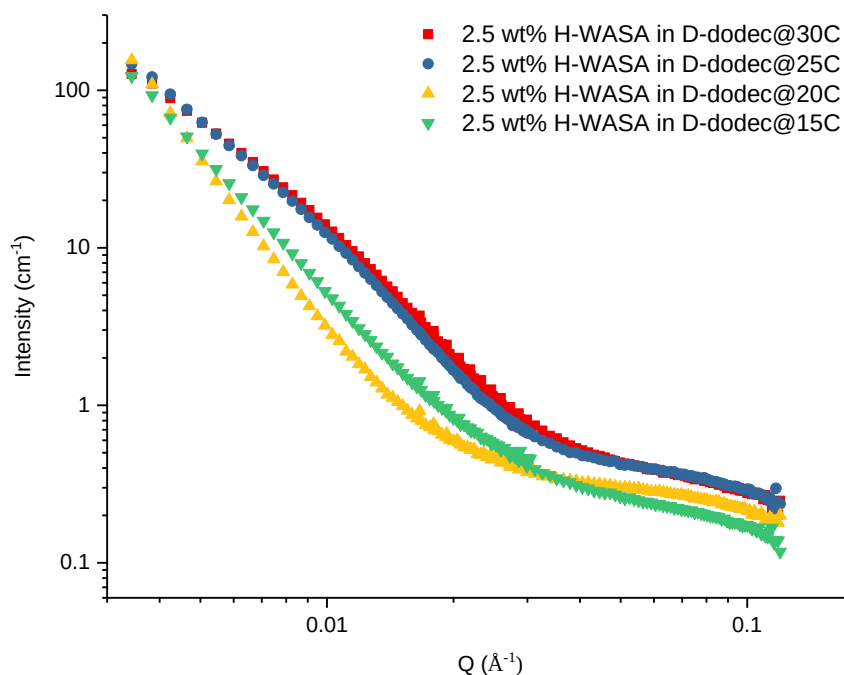


Figure 5.10: SANS data for samples of 2.5 wt% H-WASA in D-dodecane at 30, 25, 20 and 15 °C.

Figure 5.10 shows the SANS data of the 2.5 wt% H-WASA in dodecane samples at different temperatures. The lower temperatures show a slightly lower intensity than the higher temperatures but there is little difference between them. All samples were plotted on a Porod plot ($\log I(q)$ vs. $\log Q$) and linearly fitted. The gradient of this fit gives the Porod exponent and is given in Table 5.5.

Table 5.5: Porod exponent from linear fit of 2.5 wt% WASA SANS samples at various temperatures.

Sample	Porod exponent from linear fit
H-WASA in D-dodecane @ 30°C	2.6
H-WASA in D-dodecane @ 25°C	2.7
H-WASA in D-dodecane @ 20°C	3.4
H-WASA in D-dodecane @ 15°C	2.6

A Porod exponent of $2 < n < 4$ indicates a collapsed polymer chain suggesting that the WASA is behaving as a collapsed polymer coil. However, fitting the data to a specific shape and size has proved problematic. Dynamic light scattering measurements were conducted on these samples at the same temperatures to try to aid the fitting by obtaining sizes of the WASA in solution. At 30 and 25 °C a very narrow size distribution centred on 374 and 391 nm respectively was obtained. 20 °C gave a broader binary distribution centred on 292 nm and 1170 nm. 15 °C also showed a broader binary distribution centred around 181 nm and 874 nm shown in Figure 5.11.

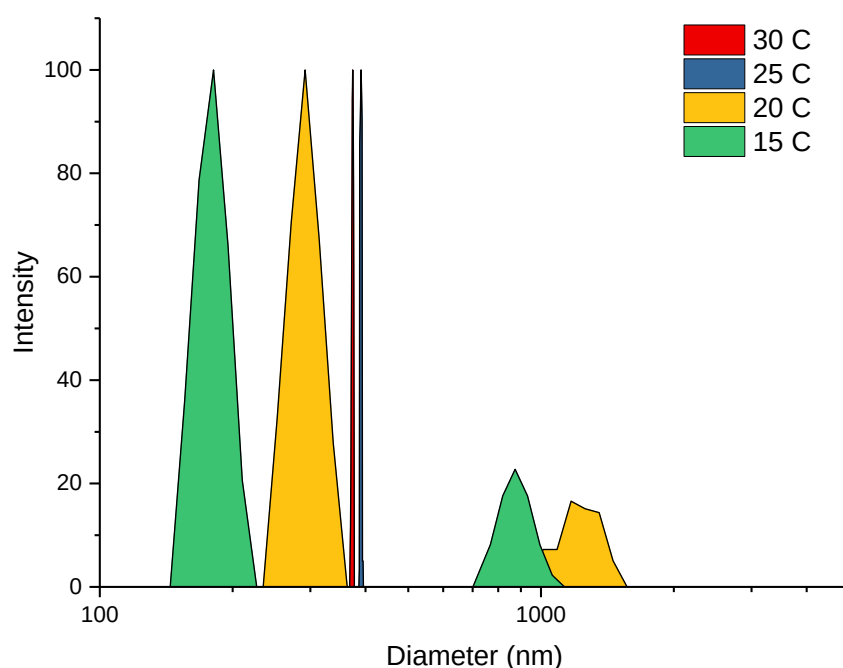


Figure 5.11: Dynamic light scattering measurements of 2.5 wt% WASA at various temperatures.

This could help to explain the reduction in scattering intensity at the lower temperatures. If the WASA is forming ~ 1000 nm structures these could settle during the SANS measurement. The broad size distributions also help to explain the difficulty in fitting the sample to a single shape and size.

5.2.3 2.5 wt% WASA, wax in dodecane

The SANS data for the model diesel with 2.5 wt% WASA at various temperatures are shown in Figure 5.13. A key to help show the different contrasts with the outer line corresponding to the plot colour is given in Figure 5.12.

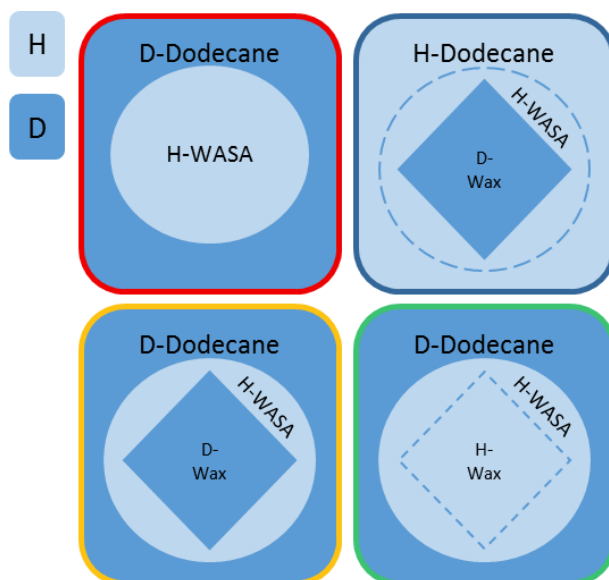


Figure 5.12: Key showing the different contrasts in 2.5 wt% WASA in model diesel SANS data. The outer colours correspond to the colour of the data plots.

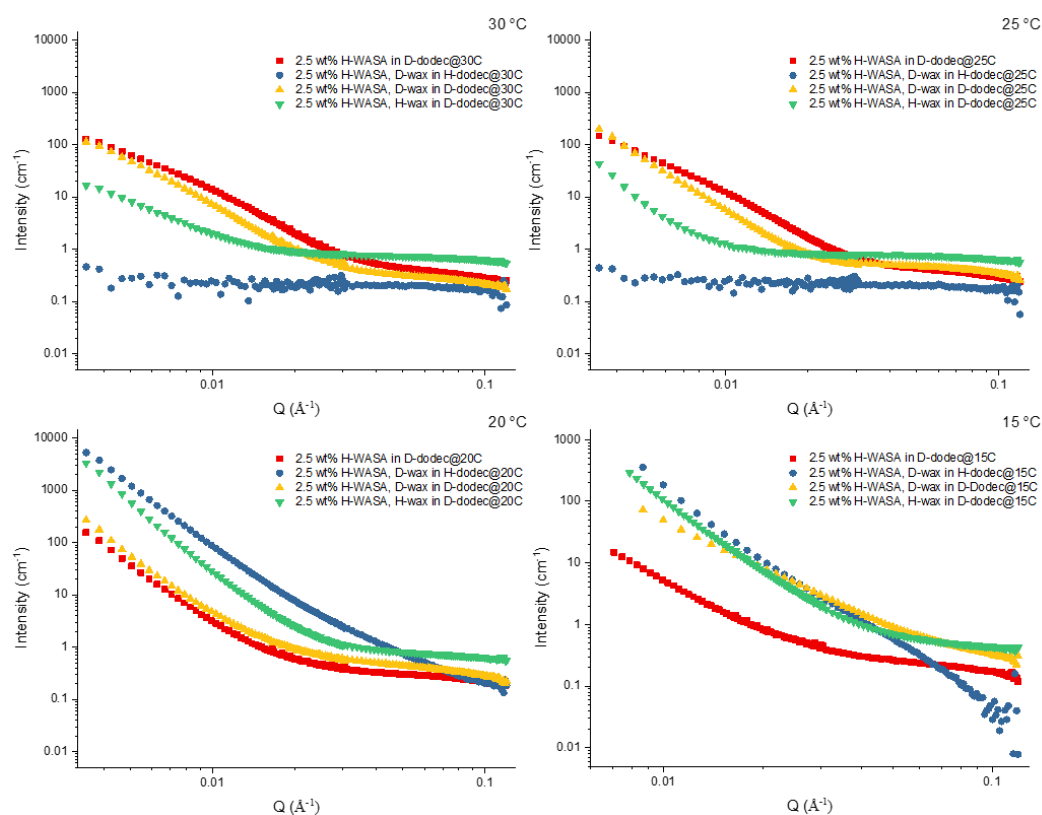


Figure 5.13: SANS data of 2.5 wt% WASA in model diesel four different temperatures and different contrasts.

The 2.5 wt% H-WASA in D-dodecane shown in red has been discussed previously in section 5.2.2. Fitting has shown that the WASA behaves as a collapsed polymer coil.

The contrast highlighting the wax (2.5 wt% H-WASA, D-wax and H-dodecane) is plotted in blue. At 30 and 25 °C (Figure 5.13) the wax is melted, and the SANS data shows very little intensity.

At 20 and 15 °C (Figure 5.13) the wax has crystallised in the presence of the WASA. Linear fitting gives a Porod exponent of ~ 4 as shown in Table 5.6. This indicates that the wax crystals are too large to be resolved and the neutrons are scattering from the wax crystal surface. However, unlike the previous wax only samples, this gradient dominates over the entire Q range and there is no gradient change at high Q . This could be due to two factors. Firstly, the WASA changes the morphology of the wax crystals to a more spherical shape thus removing the thin edge of the wax crystal plate which could be resolved by neutrons. Secondly, the WASA could disrupt the regular crystal packing of the n -alkanes and thus remove the strong unit cell scattering.

Table 5.6: Porod exponent from linear fit of 2.5 wt% H-WASA, D-wax and H-dodecane SANS samples at various temperatures.

Sample	Porod exponent from linear fit
H-WASA, D-wax and H-dodecane @ 30°C	0.1
H-WASA, D-wax and H-dodecane @ 25°C	0.1
H-WASA, D-wax and H-dodecane @ 20°C	3.6
H-WASA, D-wax and H-dodecane @ 15°C	3.8

The contrast highlighting the WASA (2.5 wt% H-WASA, D-wax and D-dodecane) is plotted in yellow. Comparing these SANS data plots to their respective H-WASA in D-dodecane plots, shown in red, show that the Porod exponents of WASA with and without wax are very similar, as shown in Table 5.7.

Table 5.7: Porod exponent from linear fit of 2.5 wt% WASA and 2.5 wt% H-WASA, D-wax and D-dodecane SANS samples at various temperatures.

Sample	H-WASA in D-dodecane Porod exponent from linear fit	H-WASA, D-wax and D-dodecane, Porod exponent from linear fit
30°C	2.6	2.7
25°C	2.7	3.1
20°C	3.4	3.3
15°C	2.6	2.5

This suggests that in the presence of the wax the WASA does not dramatically change its confirmation from a collapsed polymer coil. Due to the rigidity of the wax crystal lattice, WASA cannot have significant presence within the wax crystal without changing its morphology and thus seems to mostly be present on the surface.

The contrast highlighting the WASA and wax together (2.5 wt% H-WASA, H-wax and D-dodecane) is plotted in green. At high Q the SANS data are very similar to that of the H-WASA in D-dodecane (red plots) and H-WASA, D-wax and D-dodecane (yellow plots). At low Q the SANS data is very similar to that of the H-WASA, D-wax and H-dodecane (blue plots) with a gradient of ~ 4 . This suggests the lower Q data are dominated by the wax and the higher Q data by the WASA.

5.3 Piezo electric rheology

The SANS data appear to show large scale WASA structures in the dodecane. This could be a large gel network leading to the gelling of the wax crystal. Thus, piezo electric rheology was conducted to determine if any WASA gel networks are present. The results are shown in Figure 5.14.

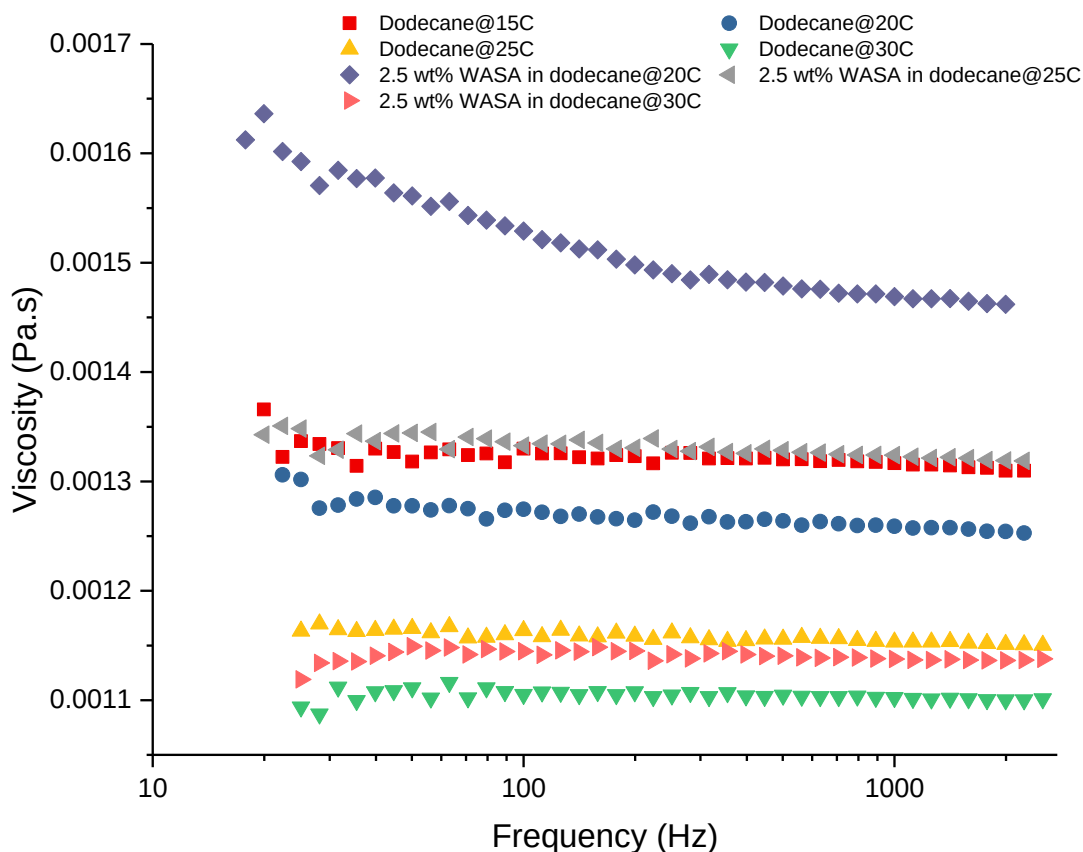


Figure 5.14: Piezo electric rheology viscosity results of dodecane and 2.5 wt% WASA in dodecane at various temperatures.

The rheology showed an increase in viscosity upon addition of the WASA to the dodecane. This is due to the WASA molecules acting as particles in the solvent. There is no evidence of any gelation or non-Newtonian behaviour. This suggests that the WASA does not form a large space scanning network and instead forms discrete large structures.

5.4 SANS2D ISIS

At ISIS the SANS2D beam line was used and set up to give a Q range of 0.00156 to 0.4909 Å⁻¹ the same banjo cells with path lengths of 5 and 1 mm were used. All samples were prepared as previously seen and hot pipetted into warmed banjo cells.

Table 5.8: Sample list for SANS2D beam run

Sample	Temperature (°C)	Additive wt%
H-WASA in D-dodecane	40, 25 and 15	1
		0.5
		0.1
H-WASA in D-dodecane	15	0.05
		0.01
H-WASA, D-wax in D-dodecane		1
H-WASA, H-wax in D-dodecane		1
H-WASA, D-wax in H-dodecane		1
H-WASA, D-wax in D-dodecane		0.5
H-WASA, D-wax in H-dodecane		0.5
H-WASA, H-wax in D-dodecane		0.5
H-WASA, D-wax in D-dodecane		0.1
H-WASA, H-wax in D-dodecane		0.1
H-C₂₂ FVA in D-dodecane	40, 25 and 15	1
		0.5
		0.1
H- C₂₂ FVA in D-dodecane	15	0.01
H-C₂₂ FVA, D-wax in D-dodecane		0.5
H-C₂₂ FVA, H-wax in D-dodecane		0.5
H-C₂₂ FVA, D-wax in D-dodecane		0.1
H-C₂₂ FVA, H-wax in D-dodecane		0.1

Data were reduced using Mantid software from the neutron beam facility and then fitted using SasView software. The SLDs used are shown in Table 5.2 the SLD of C₂₂ FVA was calculated from the monomer of the polymer.

5.4.1 WASA in dodecane

ISIS allowed lower concentrations of WASA to be used. SANS data for various concentrations of H-WASA in D-dodecane are shown in Figure 5.15 and 5.16.

At 40 °C at low Q , the large structure of the WASA is lost as the WASA is dissolved into the dodecane. However, the smaller structures, shown at high Q , are seen at all temperatures suggesting that the smaller WASA structure is present even when dissolved.

At 15 and 25 °C the SANS data is similar across the different concentrations. At low Q the large structures seen in the NIST data are present with the additional distinctive curve at high Q . Figure 5.16 shows that 0.01 wt% is too low a concentration to obtain sufficient scatter.

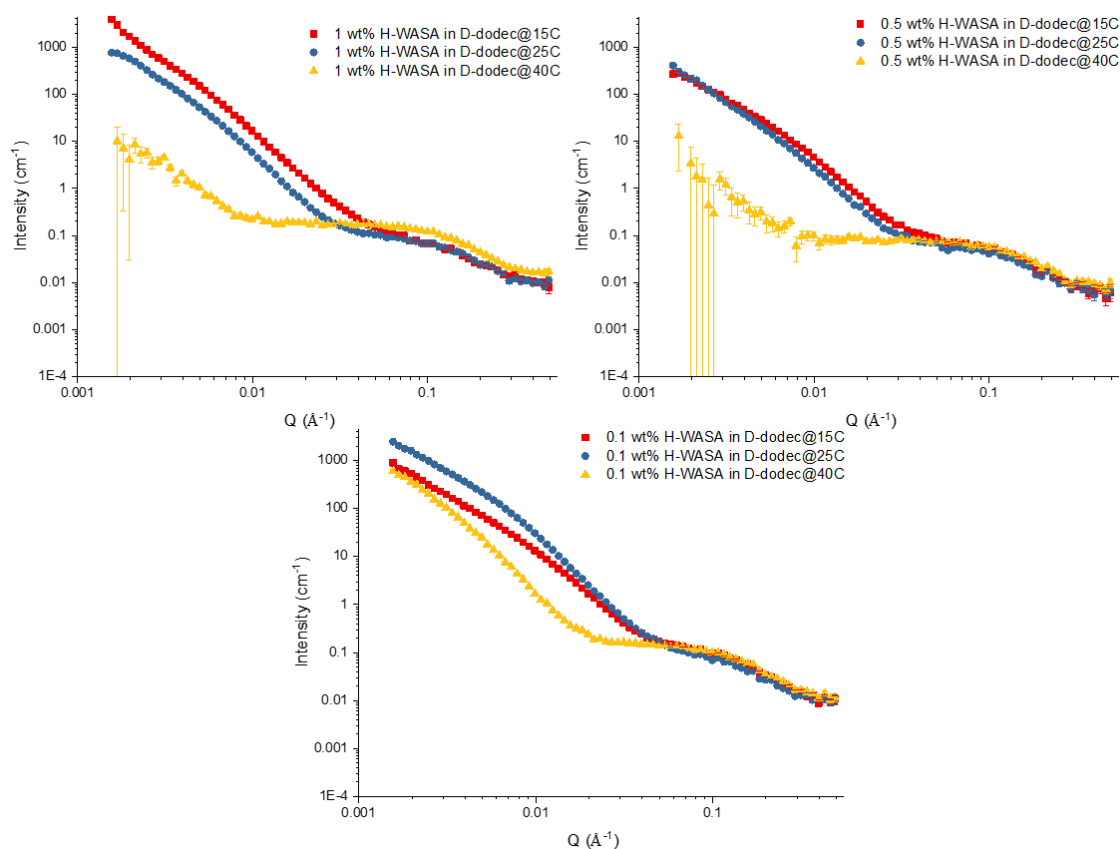


Figure 5.15: SANS data of 1 wt% (top left) 0.5 wt% (top right) and 0.1 wt% (bottom) H-WASA in D-dodecane at different temperatures.

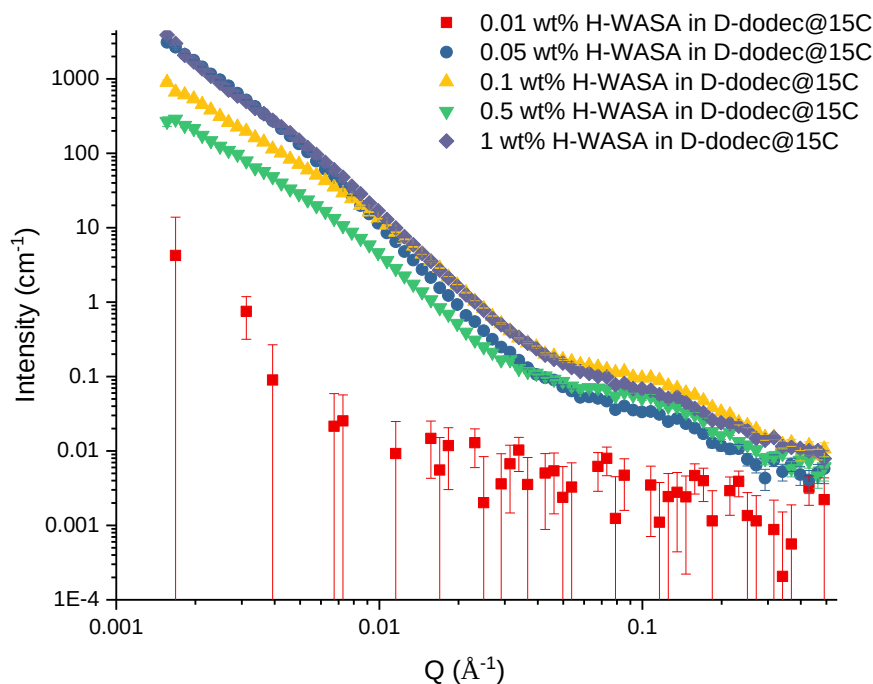


Figure 5.16: SANS data of different wt% H-WASA in D-dodecane at 15 °C.

The H-WASA in D-dodecane SANS curves show two distinct regions at low and high Q ranges above and below $0.04 \text{ \AA}^{-1}$. The Porod exponent was calculated from the linear fits separately for low Q (below $0.04 \text{ \AA}^{-1}$) and high Q (above $0.04 \text{ \AA}^{-1}$).

Table 5.9: Porod exponent from linear fit of WASA SANS samples at various concentrations and temperatures.

H-WASA in D-dodecane	Low Q ($< 0.04 \text{ \AA}^{-1}$)	High Q ($> 0.04 \text{ \AA}^{-1}$)
1 wt% @ 40 °C	2.5	1.0
1 wt% @ 25 °C	3.1	1.0
1 wt% @ 15 °C	3.1	1.3
0.5 wt% @ 40 °C	2.1	1.0
0.5 wt% @ 25 °C	2.9	1.0
0.5 wt% @ 15 °C	2.7	1.1
0.1 wt% @ 40 °C	3.4	0.8
0.1 wt% @ 25 °C	2.9	1.3
0.1 wt% @ 15 °C	2.6	1.2
0.05 wt% @ 15 °C	3.3	1.3
0.01 wt% @ 15 °C	NA	NA

The low Q Porod exponent is similar to that shown in the NIST samples and does not seem to dramatically vary with concentration. Again, suggesting a collapsed polymer coil. At high Q the Porod exponent is ~ 1 . This suggests a thin rigid rod

structure. Attempting to fit the data to a cylinder model required separate fittings for the high and low Q regions. Only the high Q region was easily fitted, for 0.5 wt% WASA @ 15°C it gave a cylinder of length 44.2 Å and radius 9.5 Å. The low Q fitting gave a cylinder of length 229 Å and radius 978 Å. However, the overlapping of the two fittings was very poor which only a very high polydispersity could rectify.

The high Q SANS data can be fit to a binary sphere model with the WASA showing small and large sphere structures. Again, the fitting of the lowest Q region is poor.

Table 5.10: SANS data fitting from binary sphere model giving sphere radii.

H-WASA in D-dodecane	Sphere Radius₁ and error (Å)	Sphere Radius₂ and error (Å)
1 wt% @ 40 °C	16 ± 0.5	9 ± 0.5
1 wt% @ 25 °C	14 ± 0.3	1014 ± 2
1 wt% @ 15 °C	15 ± 0.3	1018 ± 0.9
0.5 wt% @ 40 °C	15 ± 1.0	10 ± 2
0.5 wt% @ 25 °C	15 ± 0.4	1100 ± 300
0.5 wt% @ 15 °C	14 ± 0.4	1488 ± 1
0.1 wt% @ 40 °C	14 ± 0.1	1100 ± 200
0.1 wt% @ 25 °C	14 ± 0.5	1100 ± 400
0.1 wt% @ 15 °C	14 ± 0.4	1094.0 ± 0.7
0.05 wt% @ 15 °C	15 ± 1.0	1092 ± 0.9
Average radius	14	1125

This fitting gives two spherical structures of the WASA. One of 14 Å in radius and another 1125 Å in radius on average. The 40 °C samples do not show the larger structure which is consistent with this structure being due to the aggregation and potential precipitation/crystallisation of the WASA. 0.1 wt% WASA @ 40 °C does not follow this trend but that could be due to the sample not fully dissolving. Examples of the fitting can be seen in Figure 5.17.

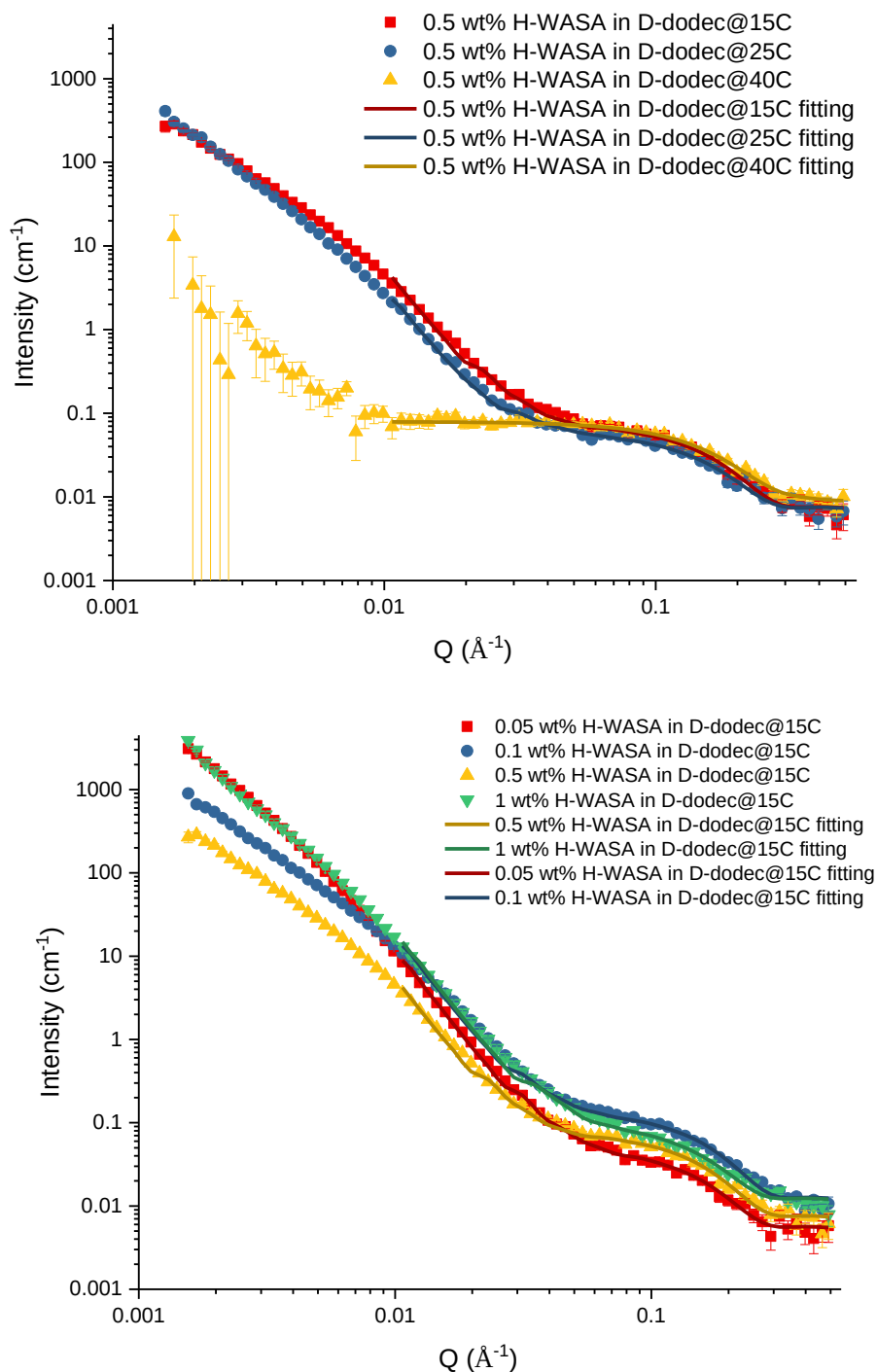


Figure 5.17: SANS data of 0.5 wt% H-WASA in D-dodecane at different temperatures with binary sphere fitting (top) and SANS data of different wt% H-WASA in D-dodecane at 15 °C with binary sphere fitting (bottom).

5.4.2 D-wax in D-dodecane

Thus far the assumption was made that D-wax in D-dodecane would give very little scatter due to the closeness of their scattering length densities, as shown in Table 5.2. To check this assumption the usual model diesel of 10 wt% wax in

dodecane was made using D-wax and D-dodecane and run in the beamline at 15 °C. The resulting SANS data is shown in Figure 5.18.

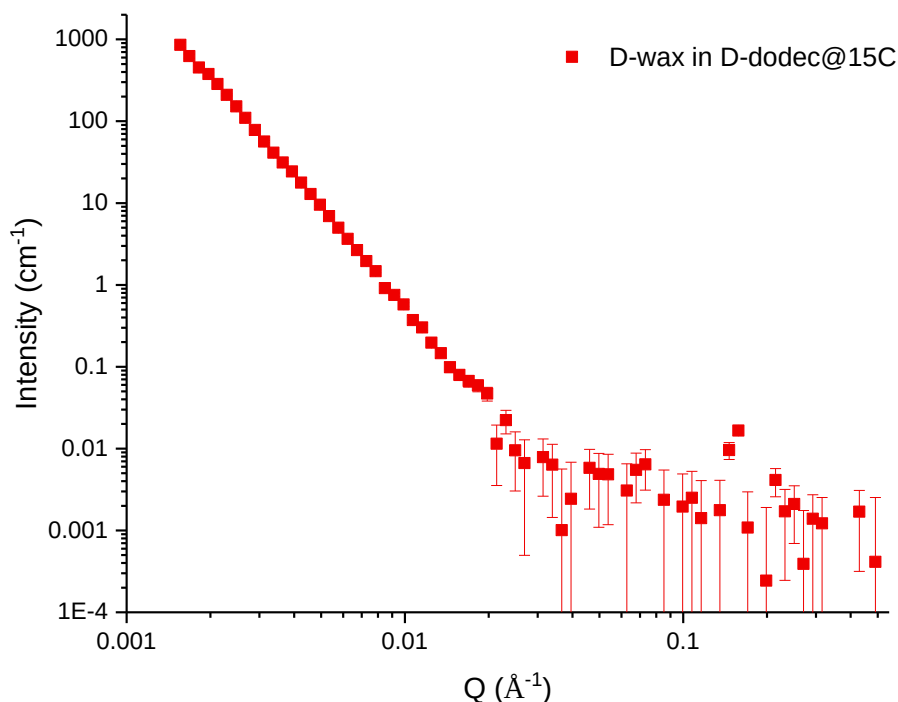


Figure 5.18: SANS data for a sample of D-wax in D-dodecane at 15 °C

Counter to our assumption this sample shows strong scattering at low Q . This is due to the large wax crystals which form. The Porod exponent from a linear fit of this scatter is 4.0 suggesting a large smooth surface. This has implications for our contrast matched samples of the additive, wax and dodecane. The scattering data of samples highlighting the additive (H-additive, D-wax and D-dodecane) will have a low Q contribution from the D-wax, probably giving the scatter a Porod exponent close to 4. However, due to the additives changing the morphology of the wax crystals we cannot assume the scatter will be the same as seen in Figure 5.18. Due to the low intensity of the D-wax in D-dodecane scatter at high Q the contrast matching assumption holds in this region.

Although not explicitly tested the contrast matching assumption that H-additive in H-dodecane would give zero scatter is also probably questionable as there is a larger difference in their scattering length densities. This should be considered when evaluating the fittings below.

5.4.3 WASA, wax in dodecane

Samples with 0.1, 0.5 and 1 wt% of WASA in the model diesel at 15 °C were also run in the beamline, the SANS curves are shown in Figure 5.19. The colours of the plots correspond to the key shown in Figure 5.12.

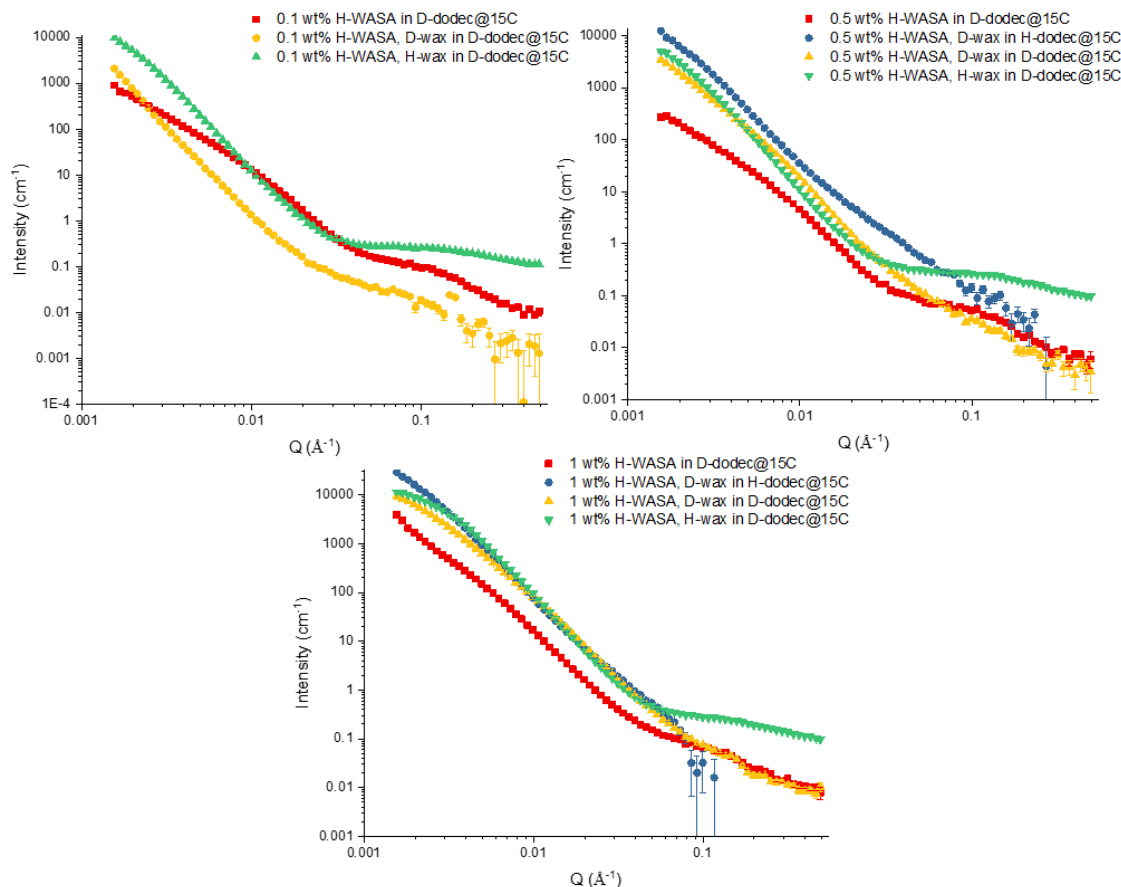


Figure 5.19: SANS data of 0.1 wt% (top left), 0.5 wt% (top right) and 1 wt% (bottom) WASA in model diesel at 15 °C and different contrasts.

The H-WASA in D-dodecane shown in red has been discussed previously in section 5.4.1. The WASA can be fitted to a binary sphere model.

The contrast highlighting the wax (H-WASA, D-wax and H-dodecane) is plotted in blue. Linear fitting gives a Porod exponent of ~ 4 as shown in Table 5.11. Like the NIST data this indicates that the wax crystals are too large to be resolved and the neutrons are scattering from the crystals surface.

Table 5.11: Porod exponent from linear fit of H-WASA, D-wax and H-dodecane SANS samples at various WASA concentrations.

Sample @ 15 °C	Porod exponent from linear fit
1 wt% H-WASA, D-wax in H-dodecane	3.4
0.5 wt% H-WASA, D-wax in H-dodecane	3.1

The Porod exponents from linear fits of the other contrasts at low Q are shown in Table 5.12. The contrast highlighting the WASA (H-WASA, D-wax and D-dodecane) is plotted in yellow. Comparing these SANS data plots to their respective H-WASA in D-dodecane plots, shown in red, show that the plots of WASA with and without the wax are slightly different. The Porod exponent of these samples increase upon the addition of the wax to the WASA. The contrast highlighting the WASA and wax together (H-WASA, H-wax and D-dodecane) is plotted in green. At low Q the SANS data is like that of the H-WASA, D-wax and H-dodecane (blue plots) with a Porod exponent of ~ 4 . However, at high Q it differs from both the H-WASA in D-dodecane and H-WASA, D-wax and D-dodecane contrast.

Table 5.12: Low Q Porod exponent from linear fit of WASA, H-WASA, D-wax and D-dodecane and H-WASA, H-wax and D-dodecane SANS samples at various concentrations.

Sample	H-WASA in D-dodecane	H-WASA, D-wax and D-dodecane	H-WASA, H-wax and D-dodecane
1 wt%	3.1	3.0	3.4
0.5 wt%	2.7	3.1	3.5
0.1 wt%	2.6	3.8	3.8

These SANS curves were fitted to a binary mixture of hard spheres with hard sphere interactions model. The smaller sphere fitting is shown in Table 5.13 and the larger in Table 5.14. The different samples give different sphere radii. IN the presence of the wax the WASA smaller sphere is increased in size and the larger sphere is decreased. The contrast highlighting both the wax and the WASA shows a decrease in both the smaller and larger sphere radii. An example of the binary sphere fitting is shown in Figure 5.20.

Table 5.13: SANS data fitting from binary sphere model giving smaller sphere radii.

Sample @ 15 °C	Sphere Radius ₁ (Å)		
	H-WASA in D-dodecane	H-WASA, D-wax in D-dodecane	H-WASA, H-wax in D-dodecane
1 wt%	15 ± 0.3	16 ± 0.6	9 ± 0.2
0.5 wt%	14 ± 0.4	17 ± 1	9 ± 0.1
0.1 wt%	14 ± 0.4	19 ± 1	9 ± 0.1
Average	14	17	9

Table 5.14: SANS data fitting from binary sphere model giving larger sphere radii.

Sample @ 15 °C	Sphere Radius ₂ (Å)		
	H-WASA in D-dodecane	H-WASA, D-wax in D-dodecane	H-WASA, H-wax in D-dodecane
1 wt%	1018 ± 0.9	804 ± 0.3	803 ± 0.4
0.5 wt%	1488 ± 1	808 ± 1	1018 ± 2
0.1 wt%	1094 ± 0.7	791 ± 7	523 ± 1
Average	1200	801	781

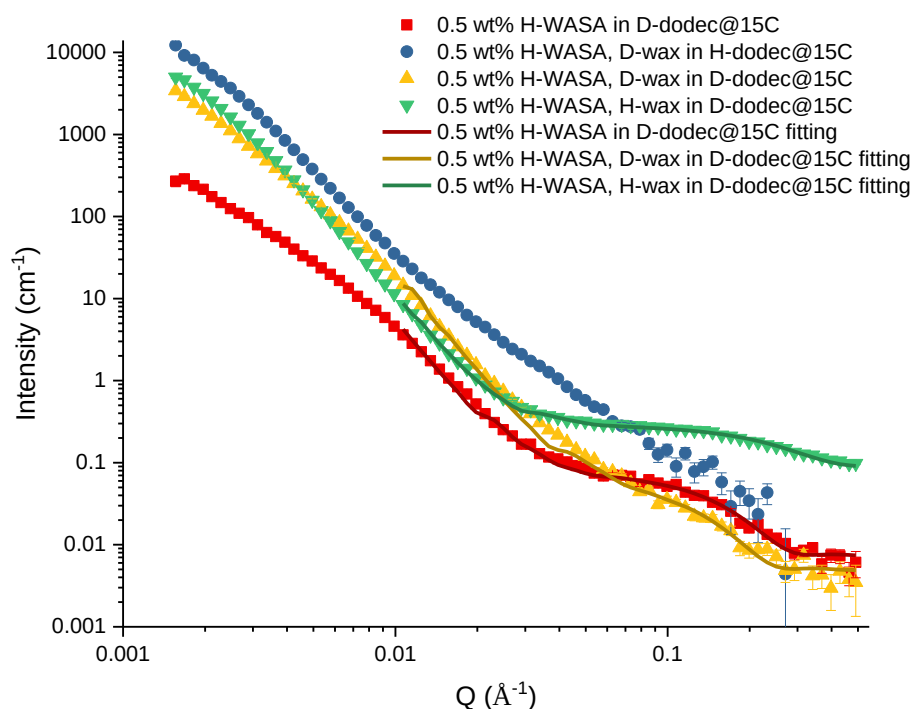


Figure 5.20: SANS data of 0.5 wt% WASA in model diesel at 15 °C and different contrasts with binary sphere fitting.

5.4.4 C₂₂ FVA in dodecane

For comparison to the WASA, C₂₂ FVA samples were also run in the beamline. SANS data from various concentrations of H-C₂₂ FVA in D-dodecane at various temperatures are shown in Figure 5.21. Due to its long alkane side chain the C₂₂ FVA copolymer behaves crystalline as shown by its sharp crystallisation peak in DSC.

At 40 °C at low Q, the large structure of the C₂₂ FVA is lost as the C₂₂ FVA is dissolved into the dodecane. At 15 and 25 °C the SANS data is very similar across the different concentrations. The SANS data shows a sharp change in gradient at $\sim 0.06 \text{ \AA}^{-1}$. Figure 5.22 shows that 0.01 wt% is too low a concentration to measure scattering.

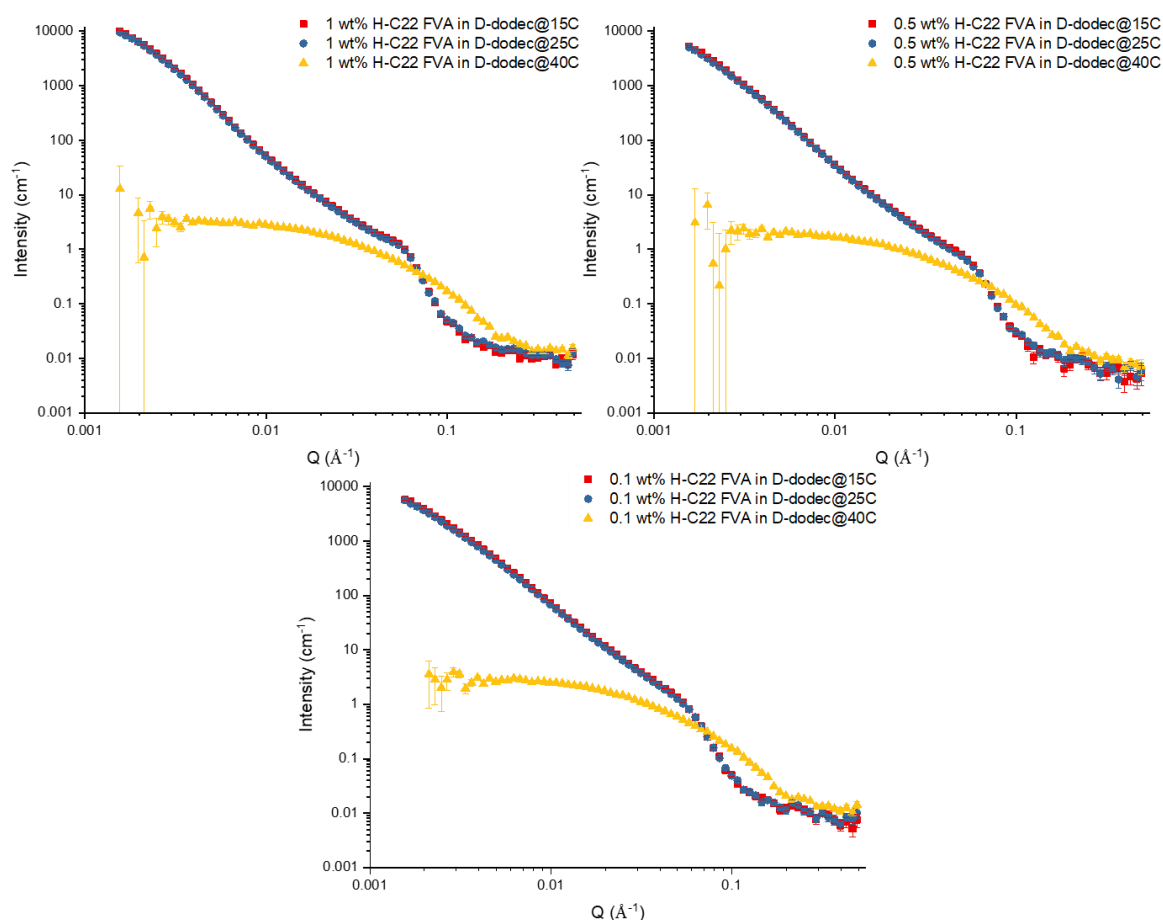


Figure 5.21: SANS data of 1 wt% (top left), 0.5 wt% (top right) and 0.1 wt% (bottom) H-C₂₂ FVA in D-dodecane at different temperatures.

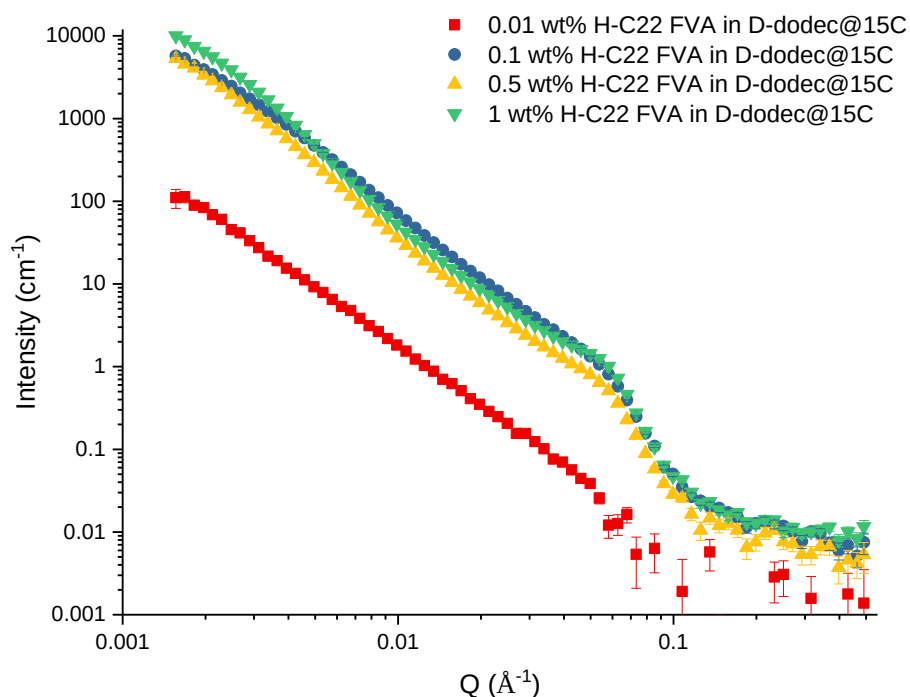


Figure 5.22: SANS data of different wt% H-C₂₂ FVA in D-dodecane at 15 °C.

The Porod exponents of the two distinct gradients of the SANS data were obtained via linear fitting and shown in Table 5.15. The change in the Porod exponents suggests a polymer network. The concentration of the C₂₂ FVA does not vary the SANS scatter as seen in Figure 5.22, thus only the 0.5 wt% is shown below.

Table 5.15: Porod exponent from linear fit of C₂₂ FVA SANS samples at various concentrations and temperatures.

H-C ₂₂ FVA in D-dodecane	Low Q	High Q
0.5 wt% @ 15 °C	2.7	0.9
0.5 wt% @ 25 °C	2.7	0.8
0.5 wt% @ 40 °C	NA	1.0

The 15 and 25 °C SANS data can be fitted to a lyotropic lamellar phase with random distribution structure (shown in Figure 5.23) the lamellar thickness is given in Table 5.16. The 40 °C can be fitted to a cylinder model the radius and length of the cylinder fitting is given in Table 5.17. An example of the lamellar phase fitting is shown in Figures 5.24 and 5.25.

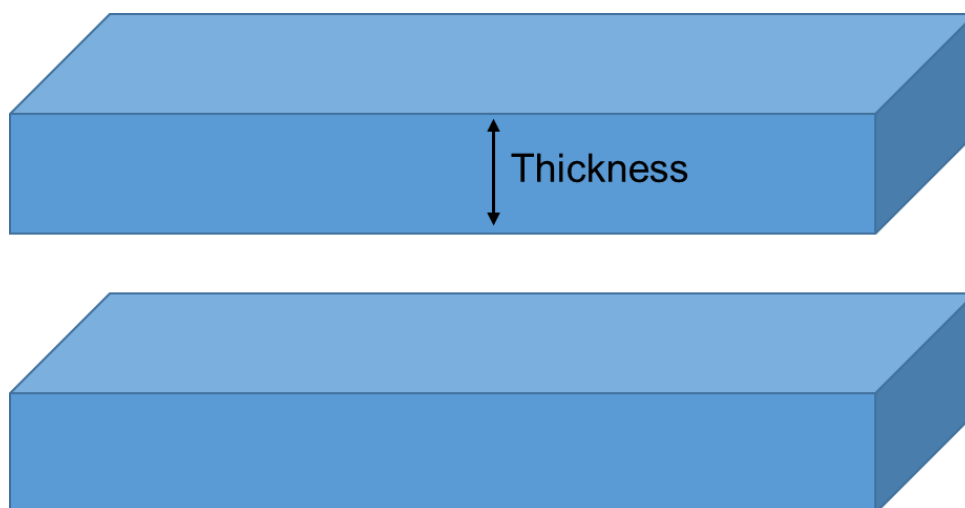


Figure 5.23: Diagram of lamellar phase showing thickness.

Table 5.16: SANS data fitting from lamellar phase model giving lamella thickness.

H-C ₂₂ FVA in D-dodecane	Lamella thickness and error (Å)
0.01 wt% @ 15 °C	59 ± 1
0.1 wt% @ 15 °C	54 ± 0.1
0.1 wt% @ 25 °C	53 ± 0.1
0.5 wt% @ 15 °C	49 ± 0.2
0.5 wt% @ 25 °C	49 ± 0.2
1 wt% @ 15 °C	43 ± 0.1
1 wt% @ 25 °C	43 ± 0.6
Average thickness	50

Table 5.17: SANS data fitting from cylinder model giving cylinder radius and length.

H-C ₂₂ FVA in D-dodecane	Radius and error (Å)	Length and error (Å)
0.1 wt% @ 40 °C	19 ± 0.1	235 ± 4
0.5 wt% @ 40 °C	20 ± 0.2	253 ± 4
1 wt% @ 40 °C	19 ± 0.5	230 ± 13
Average	19	239

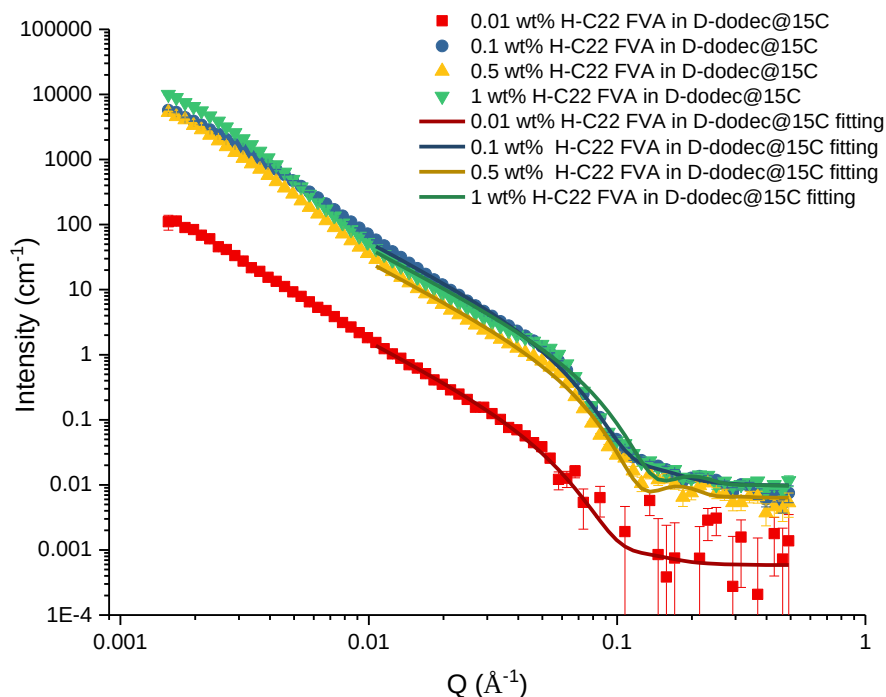


Figure 5.24: SANS data of different wt% H-C₂₂ FVA in D-dodecane at 15 °C. with lamellar phase fitting.

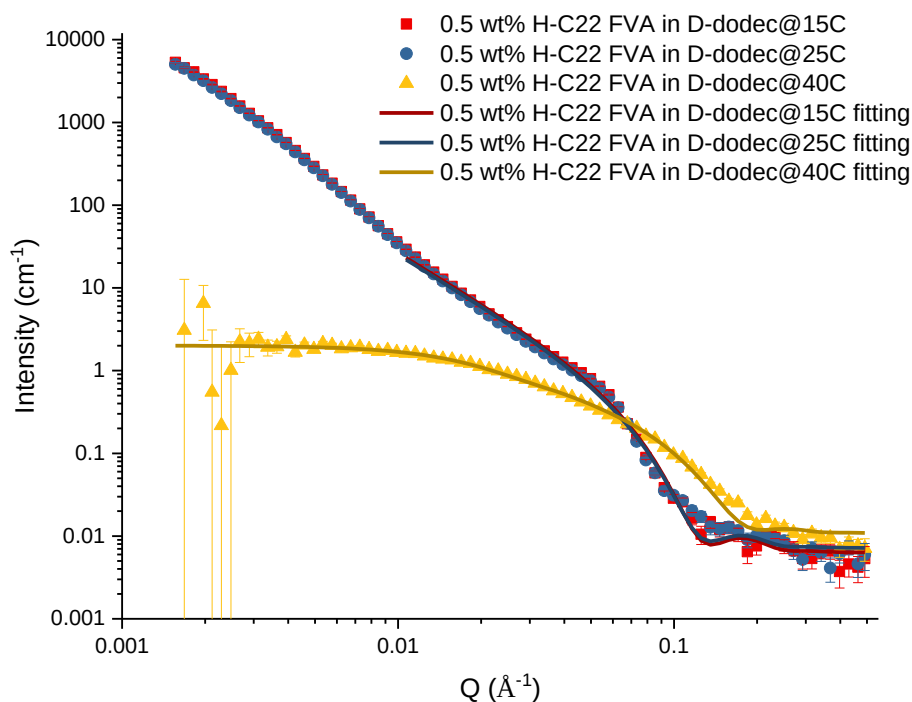


Figure 5.25: SANS data of 0.5 wt% H- C₂₂ FVA in D-dodecane at different temperatures with lamellar phase and cylinder fitting.

5.4.5 C₂₂ FVA, wax in dodecane

Samples with 0.1 and 0.5 wt% of C₂₂ FVA in the model diesel at 15 °C were also run in the beamline, the SANS curves are shown in Figure 5.26. Again, the colours

of the plots correspond to the key shown in Figure 5.12 but replacing WASA with C₂₂ FVA.

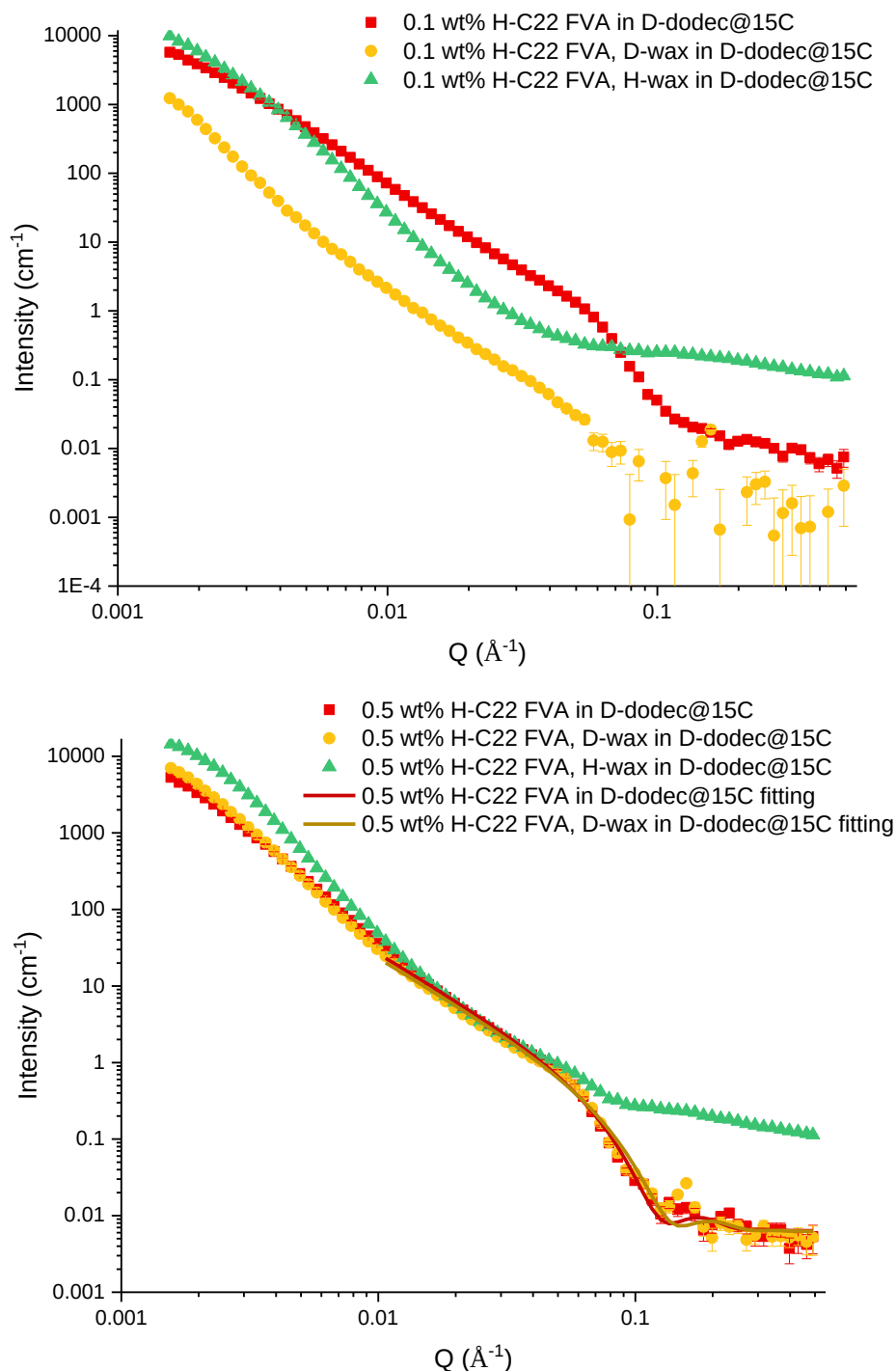


Figure 5.26: SANS data of 0.1 wt% (top) and 0.5 wt% (bottom) C₂₂ FVA in model diesel at 15 °C and different contrasts with lamella model fitting.

The contrast highlighting the C₂₂ FVA can be fitted to the lamellar phase model. The fitted lamella thickness and the C₂₂ FVA without wax lamella thickness are shown in Table 5.18. The model fittings are shown in Figure 5.26.

Table 5.18: SANS data fitting from lamellar phase model giving lamella thickness.

Sample @ 15 °C	Lamella thickness and error (Å)	
	H-C ₂₂ FVA in D-dodecane	H-C ₂₂ FVA, D-wax in D-dodecane
0.5 wt%	49 ± 0.2	44 ± 0.2
0.1 wt%	54 ± 0.1	73 ± 1
Average	51	59

There is also a small peak seen in the H-C₂₂ FVA, D-wax and D-dodecane in both 0.1 and 0.5 wt% and in 0.1 wt% H-WASA, D-wax and D-dodecane shown in Figure 5.27. It is also found in D-wax in D-dodecane at $Q = 0.158 \text{ Å}^{-1}$ which corresponds to a length scale of 40 Å, because it is found at high Q and such peaks are not seen in any other it is likely to be due to the D-wax when there is very low scattering intensity at low Q .

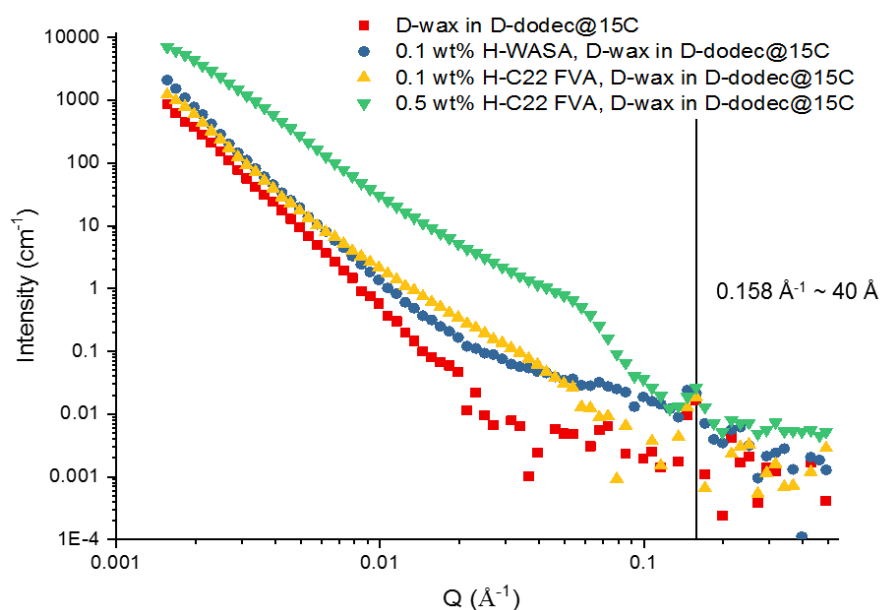


Figure 5.27: SANS data of 0.1 and 0.5 wt% of H-C₂₂ FVA, D-wax and D-dodecane and 0.1 wt% H-WASA, D-wax and D-dodecane at 15 °C with a line showing the peak.

5.5 BT5 USANS NIST

The BT5 USANS beamline gave a Q range from 5.55×10^{-5} to $2.66 \times 10^{-3} \text{ \AA}^{-1}$ from 6 motor positions. The samples ran in BT5 at NIST are listed in Table 5.19 along with background samples of D-dodecane and H-dodecane. The samples were prepared exactly as described for the NG7 experiment. To ensure a good signal to noise ratio, each sample scatter needs to be at least an order of magnitude larger than the background D or H-dodecane scatter. This limits lower Q -ranges of usable data and the cut off points are shown in Table 5.19. NA indicates that the sample scatter was too weak to be useable, this is the case at high temperatures where the sample is dissolved.

Table 5.19: Sample list run on BT5 SANS beam run

Sample	Additive wt%	Temperature (°C)	Lower Q limit ($\text{\AA}^{-1}$)
H-WASA in D-dodecane	2.5	30	NA
		20	NA
		15	2.97E-05
H-wax in D-dodecane	0	20	2.32E-05
		15	2.35E-05
H-WASA, H-wax in D-dodecane	2.5	30	NA
		20	2.86E-05
		15	3.09E-05
H-WASA, D-wax in D-dodecane	2.5	30	NA
		20	2.62E-05
		15	2.63E-05

The only full set of data we obtained is for 15 °C. This set of USANS data is plotted in Figure 5.28.

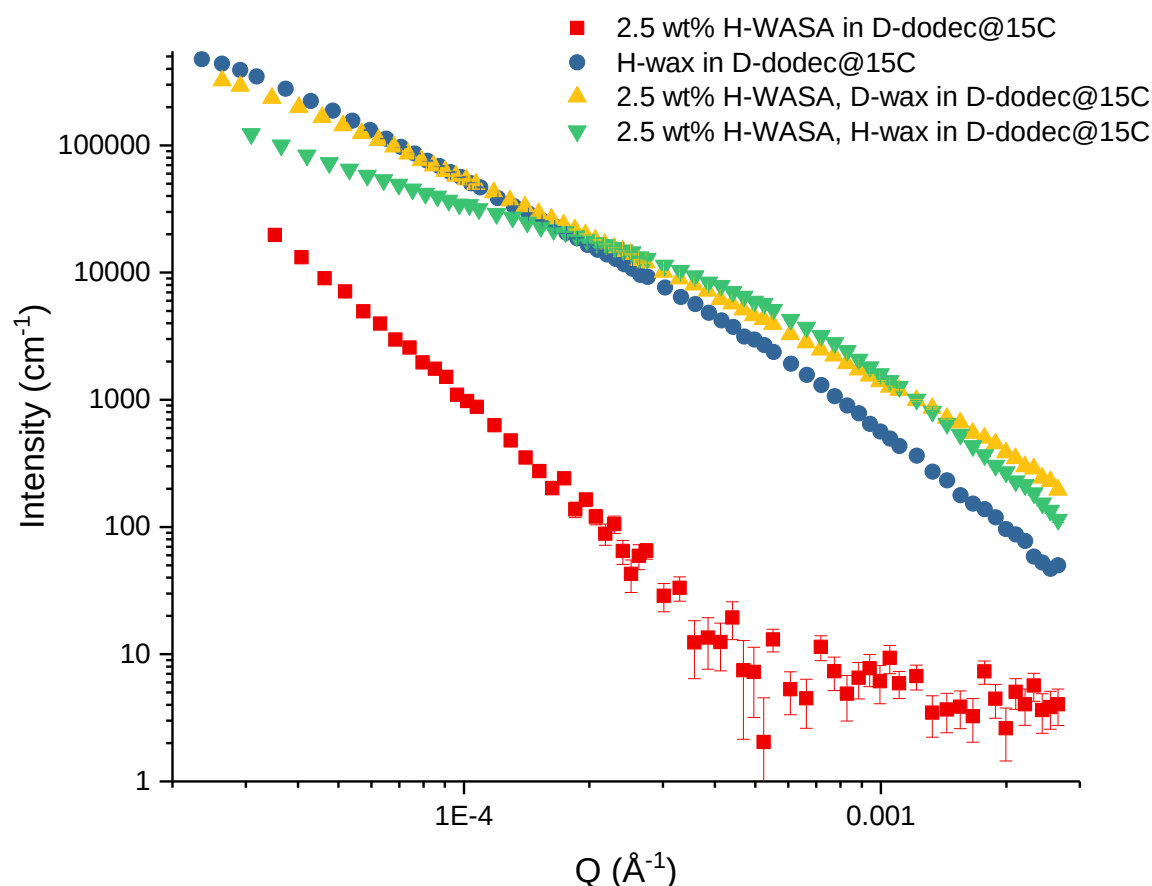


Figure 5.28: USANS data of H-WASA in D-dodecane, H-wax in D-dodecane and 2.5 wt% WASA in model diesel at 15 °C in different contrasts.

Data were reduced using Igor software from the neutron beam facility and then fitted using SasView software. The SLDs and instrumental slit smearing (height – $0.022 \text{ \AA}^{-1}$, width – $2.25 \times 10^{-5} \text{ \AA}^{-1}$) must be inputted into the fitting software. Again, the Porod exponents were calculated via the Guinier Porod function and are shown in Table 5.20.

Table 5.20: Porod exponent from Guinier-Porod fit of USANS samples at 15 °C.

Sample	Porod exponent from linear fit
H-WASA in D-dodecane @ 15°C	4.2
H-wax in D-dodecane @ 15°C	2.9
H-WASA, D-wax and D-dodecane @ 15°C	2.6
H-WASA, H-wax and D-dodecane @ 15°C	3.7

Fitting the USANS data to previously used models does not give smooth fits. H-WASA in D-dodecane fits nicely to a sphere model of radius $5 \pm 0.06 \text{ \mu m}$. This large size suggests phase separation of the WASA from the dodecane which is understandable due to its low solubility and the long time needed to collect the

USANS data. The H-wax in D-dodecane USANS data does not smoothly fit the same cylinder model used in section 5.2.1. The fit gives a diameter of $1091 \pm 1 \mu\text{m}$ and length $1 \pm 0.001 \mu\text{m}$, both are shown in Figure 5.29. The H-WASA, D-wax and D-dodecane and H-WASA, H-wax and D-dodecane USANS data did not fit to binary sphere, cylinder or sphere models.

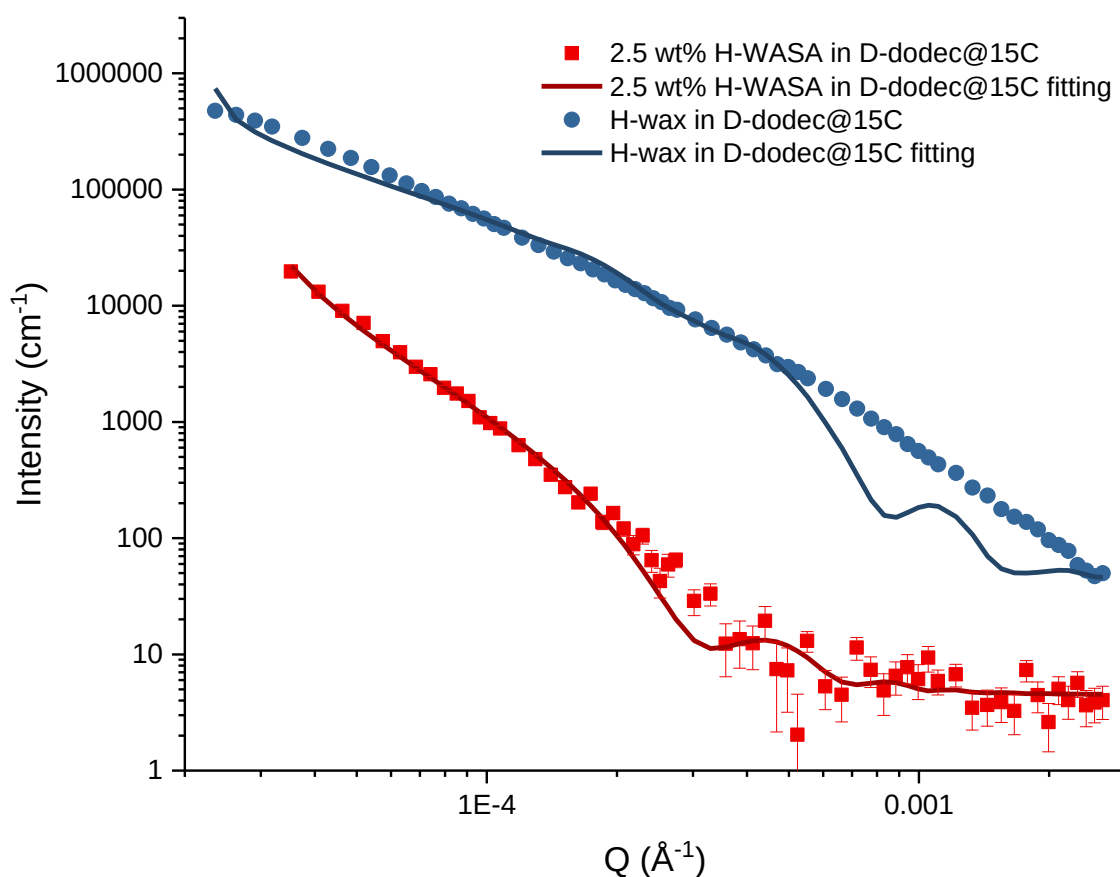


Figure 5.29: USANS data of H-WASA in D-dodecane and H-wax in D-dodecane 15 °C with fittings.

5.6 Interfacial tension measurements

The interfacial tension of a water drop in dodecane with increasing concentration of WASA was measured *via* the pendant drop method. This was to determine the extent of the role of water in the system and the interfacial action and surfactant properties of WASA. The literature value for the water interfacial tension in dodecane is 52.7 mN m^{-1} and is depicted in the results graph by a dashed line shown in Figure 5.30.

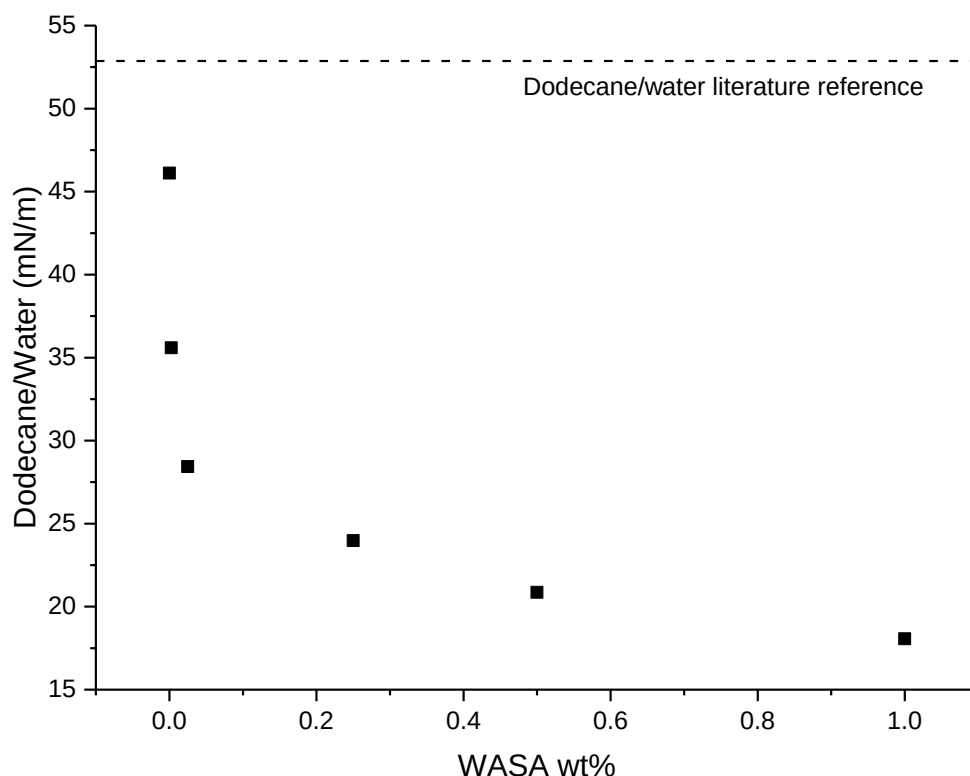


Figure 5.30: Interfacial tension of a water drop in dodecane with increasing concentration of WASA was measured by pendant drop.

The dodecane used for the experiment was not anhydrous and not purified before use. This is the reason the dodecane/water interfacial tension is lower than the literature value. Upon addition of as little as 0.0025 wt% WASA the interfacial tension is decreased by 10 mN m^{-1} at 0.5 wt% addition of WASA the interfacial tension is halved. This suggests that WASA has a significant presence at the interface and behaves as a surfactant. It also suggests that any water in the diesel could affect the WASA behaviour.

6 Discussion

6.1 Model Diesel and Location of WASA

6.1.1 Designing model diesel

The additives do not appear to affect the crystallisation of single *n*-alkanes enough to prevent the growth of large wax crystals and the formation of a gel. This could be due to the rigidity of the single *n*-alkane crystal structure, not allowing the additives to co-crystallise with or incorporate into the wax crystal to modify its structure.

Roberts *et.al.*,¹⁸ used high-resolution synchrotron x-ray powder diffraction to characterise *n*-alkane crystals. They showed that mixing large ranges of *n*-alkane chain lengths increased the amount of disorder in the inter-lamellae region between chain layers (Figure 6.1). Differences of just a few carbon atoms can cause protrusions into the inter-lamellae region. These chain ends can twist and bend, as they are no longer held by van der Waals constraints. This suggests that the large range of chain lengths in diesel leads to a large amount of disorder in the inter-lamellae region, which disrupts packing and hinders further nucleation along that plane. The system compensates by inter-chain mixing, which pushes the lamellae apart and thus produces kinks along the carbon backbone. This disorder found in crystals of multiple *n*-alkane could be the reason why the additives can affect the crystallisation of the multiple *n*-alkane crystals but not the single *n*-alkanes crystals.

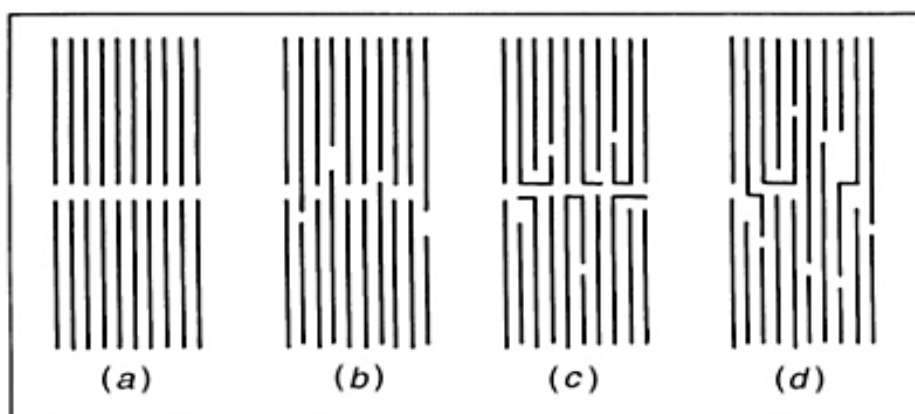


Figure 6.1: Schematic of inter-lamellae packing for a single *n*-alkane and increasingly high variance mixture of *n*-alkanes, showing the increasing disorder at the lamella interface. Diagram reproduced from reference ¹⁸.

6.1.2 Effect of additives on model diesel

Upon addition of WASA to the model diesel 3 key effects can be observed;

1. The wax crystals settle slowly as opposed to gelling like the un-doped model diesel.
2. The wax crystal size is reduced and the distribution of sizes narrowed.
3. The wax crystallisation temperature, T_c , is reduced.

Increasing the wt% amount of WASA in the system increases these effects. The change in the shape of the DSC crystallisation peak trace upon addition of the WASA indicates that the WASA is incorporating into the wax crystal rather than just acting upon it by being present in solution. Additionally, the eutectic data shows that the decrease in T_c seen upon addition of WASA in the model diesel is not due to eutectic mixing and is a stronger effect.

The evidence of chain matching between the *n*-alkanes and WASA further supports this. If the WASA decreased the T_c of all alkanes equally this would imply a non-specific interaction between the alkane and WASA. However, as the WASA decreases the T_c of alkanes with a similar chain length more, it must have a specific, strong interaction with the wax.

A plateau in effects is reached around 2.5 wt%, where any additional WASA does not seem to have any additional effect. This could suggest that the wax crystals become saturated with WASA and thus any more WASA is just present in solution and does not act upon the wax.

6.1.3 Location of WASA

The mechanism of WASA action will be highly dependent on its position in the wax crystal. If the WASA is spread throughout the bulk of the wax with no strong surface presence the anti-settling effect could be attributed to the decrease in the wax crystal size and thus settling speed. If it has a strong surface presence this may suggest other methods causing gel formation, as discussed in section 1.6.

The lower solubility of the WASA compared to the alkanes determined by the van't Hoff method suggests that the WASA could be present throughout the whole wax crystal, as it could be present at the nucleation and growth of the wax crystal. DSC testing shows no indication that the WASA acts as a nucleator but it could incorporate itself into the wax crystal during the crystal growth stage. If this

happened we could expect to see changes in the x-ray powder diffraction spectra between the doped and un-doped wax crystals, as the wax crystal lattice should have to alter to incorporate the WASA. The diffraction patterns showed very little difference between the wax crystals with and without WASA. Suggesting that the WASA is not significantly altering the wax crystal lattice. It could always be argued that the instrument could not detect subtler changes occurring due to the WASA presence and a synchrotron source should be used. However, this experiment suggests that the WASA is not significantly altering the wax crystal lattice and may be on the surface of the wax crystal.

Infra-red spectroscopy confirms that WASA is present in the wax from the model diesel. It also showed that the WASA is present in the wax at much greater quantities than it is in the surrounding dodecane solution. However, the exact amount located in the wax vs the solution could not be calibrated. The more sensitive DRIFTS-IR also showed presence of the WASA in the wax suggesting that the WASA is present on or near the wax surface. However, its spectra could not be directly compared to that of the ATR-IR.

X-ray photoelectron spectroscopy (XPS) depth profile scans show a higher presence of oxygen on the surface of the WASA doped wax crystals. This is not due to contamination because the wax crystals with no WASA give no oxygen peak at any of the etching times. Notably only the anion of the WASA contains oxygen so this cannot account for the full WASA salt. It suggests that on average at a depth of 56 Å (68 s etching time) only half of the original amount of oxygen is present. This trend is not repeated by nitrogen and the data is very scattered. However, nitrogen is commonly much more difficult to detect than oxygen as the peaks are noisier and lower in intensity. Overall, XPS results suggest that the WASA is more prominent on the surface of the wax crystal.

6.1.4 Other additives

C₂₂ FVA, AOT and two ionic liquids, PC₄.Cl⁻ and [BMiM][NtF₂] were doped into the model diesel, to see their effects on the wax crystals using optical microscopy, DSC and IR-spectroscopy. The C₂₂ FVA reduced the wax crystal size, the crystallisation temperature, T_c , and showed a strong presence on the wax crystal. The other additives showed no effect on the wax crystals. This demonstrates that the molecular design of cold flow additives like WASA and C₂₂ FVA is very important. Cold flow additives need to be able to strongly associate with the wax

crystal for them to change the morphology and lower the T_c . Key attributes to a successful cold flow additive include long alkane chains, to chain match with the diesel alkanes, a chain conformation that allows incorporation into the wax crystal lattice and a functional group imparting the desired effect.

6.2 How Does Anti-Settling Occur?

6.2.1 Electrophoresis

Electrophoresis experiments show that the wax crystals have a positive charge in the presence of WASA. While, un-doped model diesel and C₂₂ FVA doped wax crystals show no charge. The electrophoretic effect is only seen in the presence of WASA. Even at very low 0.01 wt% doping the WASA still imparts a charge to the wax crystals. We have shown that the WASA is incorporated onto the wax crystal thus the WASA salt must dissociate to impart this positive charge. We have several possibilities as to how the WASA could impart this charge (shown in Figure 6.2);

1. The WASA dissociates in solution. The wax precipitates and preferentially co-crystallises with the WASA cation. The WASA anion remains in solution either molecularly or in micelles.
2. The WASA does not dissociate in solution. The wax precipitates and promotes complete dissociation of the WASA by preferentially co-crystallising with the WASA cation and rejecting the anion. The WASA anion remains in solution either molecularly or in micelles.
3. The WASA does not dissociate in solution. The wax precipitates and promotes partial dissociation of the WASA by preferentially co-crystallising with the WASA anion and rejecting the cation. The WASA cation remains on the surface of the wax crystal imparting a positive charge.

The voltage required to observe the electrophoretic effect was also investigated. A weak repulsion from the anode was observed at 25 V cm⁻¹. The effect is strengthened as the voltage is increased. Below 25 V cm⁻¹ no effect is observed. This could be due to the large size of the electrophoresis cell and concentrated presence of wax crystals obscuring movement. A smaller cell and diluted model diesel could potentially show effect at lower voltages, see section 7.2. Additionally, this suggests another theory for the charge (shown in Figure 6.2);

4. The WASA does not dissociate in solution. The wax precipitates and promotes partial dissociation of the WASA by preferentially co-crystallising with the WASA cation. The WASA anion remains on the surface of the wax crystal. A strong enough voltage promotes enough dissociation of the cation and anion to impart a charge to the wax crystal.

Previous work on lattice chain matching,⁴⁷ asserts that the WASA anion would be preferably adsorbed to the crystal surface rather than the cation, as discussed in section 1.5.3. If true this discounts theories one, two and four. The ions must be at least partially separated to provide any sort of surface charge to the wax crystals. Therefore giving a fifth theory similar to theory three;

5. The WASA anion is adsorbed to the crystal, generating a partial dissociation from the cation. The WASA cation is not sufficiently dispersed in the surrounding fuel and remains near the negatively charged wax surface. This creates a positively charged shell around the wax crystal causing the wax crystals to be attracted to the negative electrode.

This is similar to electrostatic layer-by-layer (LbL) adsorption (also called layer-by-layer polyelectrolyte deposition) where a capsule is formed by the sequential addition of oppositely charged polymers, the last layer leaving a charged shell around the capsule.^{94,95}

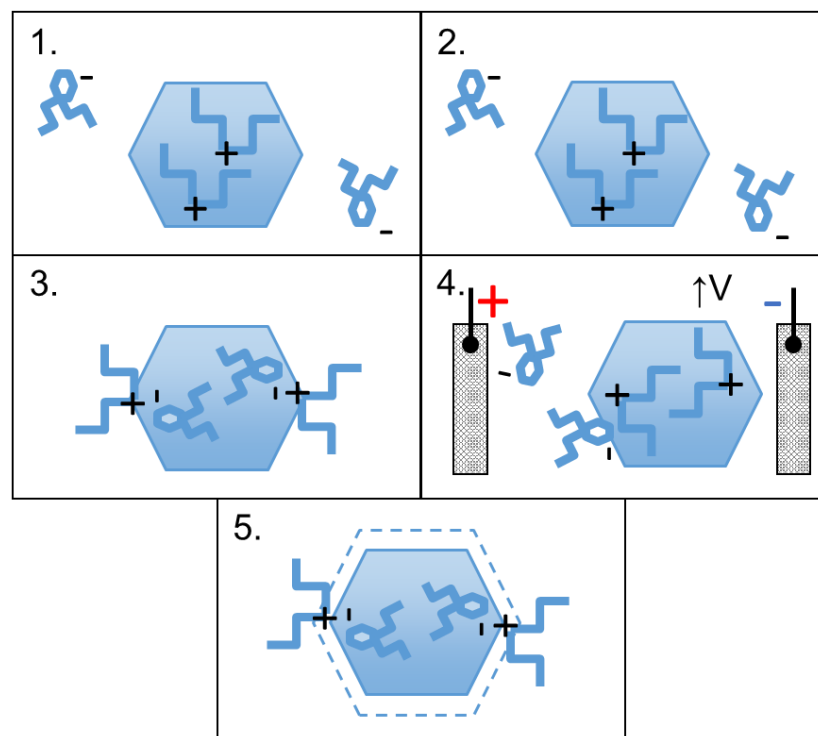


Figure 6.2: Diagrams depicting the ways in which WASA could impart charge to a wax crystal.

Adding organic salt was effective in screening the charge imparted to the wax crystals from the WASA. This shows that this is an electrostatic effect as opposed to an experimental error. However, screening could occur in any of the scenarios described above.

Conductivity testing showed no correlation between WASA concentration and conductivity. At 2.5 wt% WASA the conductivity observed was only slightly above that of analytical standard Sigma-Aldrich dodecane used in the model diesel which contains on the order of 10 to 100 ppm water contamination. This suggests we can rule out the WASA dissociating in dodecane and theory one. Thus, the dissociation and charge must be caused by the WASA incorporation onto the wax crystal.

The electrostatic contribution to colloidal dispersions in non-aqueous media, such as wax crystals in fuel is not fully developed. A simple extension of DLVO theory to non-aqueous dispersions by Lyklema suggests a slow decay of the potential through the double layer so repulsion of charged colloids is low but long range.⁹⁶ Albers and Overbeek argued that due to the slow decay of the potential, the net potential as the double layers overlap varies slowly with distance and thus double layer effects alone are not enough to stabilise a highly concentrated hydrocarbon suspension.⁹⁷ Thus, for WASA to provide electrostatic stabilisation its ions must be separated by strong forces such as the crystallisation of one ion preferentially over the other. In reality there is likely to be an equilibrium distribution between ion pairs and free ions.⁹⁸

These electrophoresis experiments suggest that the mechanism of wax anti-settling of the WASA could be due to electrostatics causing an electrostatically induced repulsive weak gel. This can further be explored using rheology.

6.2.2 Rheology

Comparing compressional and oscillatory rheology gave similar G_0 parameters suggesting that wax alignment is not an issue and oscillatory rheology is a good technique to study the wax gels as shown in Figure 6.3.

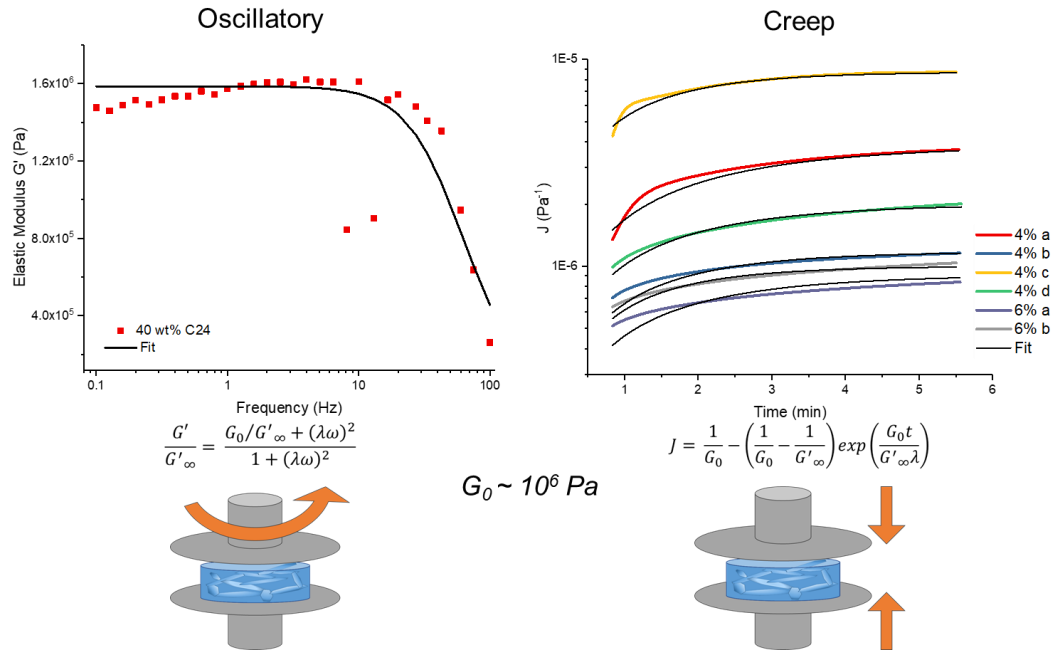


Figure 6.3: Diagram showing the results of oscillatory and creep testing on 40 wt% C₂₄, the models used to compare between the different rheological methods and the common result of $G_0 \sim 10^6 \text{ Pa}$.

First, the effect of changing the amount of wax in the model diesel was studied. Increasing the volume fraction of wax increased the gelation temperature and elastic modulus, G' , of the gel. This result is logical as the higher the volume fraction of the alkanes, the higher the system lies on the solubility line and thus the crystallisation temperature and consequently the gelation temperature is increased, see section 1.4.

Gelation occurs in the model diesel when the wax crystals interact to form volume-spanning networks which trap the remaining dodecane in a house of cards structure depicted in Figure 6.4. The higher the volume fraction of the wax the stronger this volume spanning network becomes.

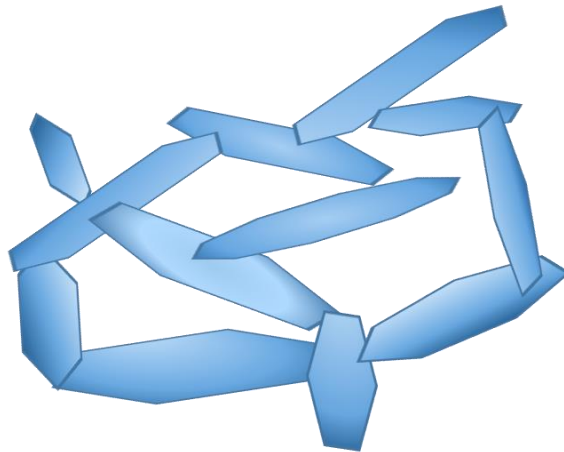


Figure 6.4: Diagram of wax crystals forming a volume spanning network.

The effect of WASA, EVA, C₂₂ FVA and the organic salt at different concentrations on the 10 wt% model diesel was investigated. The organic salt was added to elucidate the role electrostatics plays in the gelation effect of the WASA.

The gelation temperature followed the trends shown in crystallisation temperatures measured by differential scanning calorimetry (section 3.2.1.2). The model diesel gelled at 24 °C. The addition of additives did not vary this gelation temperature more than $\pm 3^\circ\text{C}$. The addition of lower amounts of C₂₂ FVA reduced the gelation temperature. The addition of EVA did not change the gelling temperature. The addition of WASA and organic salt behaved similarly and did not reduce the gelation temperature.

The effect of the additives on the strength of the gel was the most interesting set of rheology experiments. Figure 6.5 shows the effect of under 1 wt% additive doping on the wax crystal morphology. The gel caused by the large rhombic wax crystal plates of the un-doped model diesel was removed as the additives reduce the size of the wax crystals.

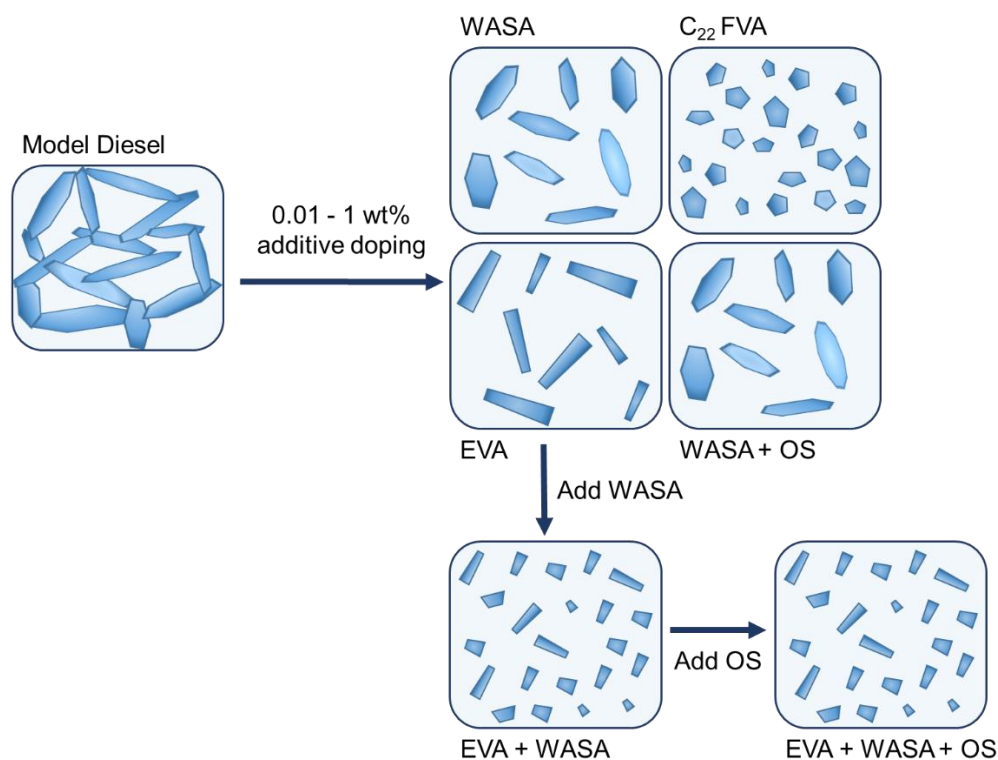


Figure 6.5: Schematic depicting change in wax crystal morphology in the presence of different additives and additive combinations

A solution of model diesel with 1 wt% WASA still gels despite the smaller size of the wax crystals (shown in Figure 3.7). If this gel is caused by electrostatics, the

addition of the organic salt to this system should significantly weaken the gel. However, upon the addition of organic salt the gel is only slightly weakened, not as much as would be expected if the gel was purely electrostatic in nature.

To try to eliminate the aspect of gelling caused by the morphology of the wax crystals, and solely study the gelling due to the WASA, 0.01 wt% EVA was added to the systems with 1 wt% WASA with and without 1 wt% organic salt. Both systems gave a gel slightly stronger than the 1 wt% WASA gel. This demonstrates that the WASA is causing the gel as opposed to the wax crystal morphology.

These rheological results rule out a simple repulsive electrostatic gel being the means of WASA action and challenges the conclusions drawn from the electrophoresis experiments. The WASA must be causing the gelation in a different or more complex way.

6.2.3 Settling testing

Work was started to devise a simple way to study the settling of the wax crystals, improvements on this experiment are found in further work. Samples showed an initial quick settling and then a slower secondary settling. The initial and secondary settling were generally faster than the calculated Stokes settling velocity.

6.3 Structure of WASA

6.3.1 SANS samples

The solubility and crystallisation temperature data gave temperature ranges in which we could work in during the SANS runs. They also indicted what we could expect to scatter at different temperatures. However, it is important to note that due to beamline constraints the heating and cooling of samples was not specially controlled, nor the time samples spent at temperatures. This was considered when analysing SANS results.

The change in effect between H and D versions of WASA is stark. Unfortunately, due to constraints in synthesising, more deuterated WASA versions could not be produced for further experiments. Both deuterated WASA versions lacked the ability to reduce the crystallisation temperature of the wax crystals or change their morphology. In the DSC traces both showed crystallisation peaks at temperatures above the wax or H-WASA crystallisation. Optical microscopy also shows the

presence of dark needle-like crystals not previously observed. This suggests that the D-versions of the WASA are less soluble in the model diesel and that it crystallises out of solution at a high temperature rather than incorporating or co-crystallising with the wax. Both the deuterated (D-ring and side chains) and the partially deuterated (just D-ring) WASA show similar crystallisation temperatures around 39 °C. This suggests that the substitutions on the ring that are the main driving factor for the lower solubility. This could be due to the deuterium changing the ability of the aromatic ring to hydrogen bond and solvate in the dodecane.⁹⁹ It could also be due to the D-WASAs having a slightly higher molecular weight.

6.3.2 NG7 SANS NIST

This NIST SANS beam runs where conducted with 2.5 wt% WASA samples as lower concentrations did not give enough scatter in reasonable acquisition times. Wax only samples fit nicely to a cylinder model with sizes corresponding to microscope observations. Fitting of WASA only samples suggested a collapsed polymer coil and DLS of the samples gave a broad size distribution. This explains why there was difficulty fitting the WASA to a single size and shape. Additionally, the piezo electric rheology ruled out WASA forming a large space scanning network and instead it seems to form discrete large structures.

In the 2.5 wt% doped model diesel the WASA scatter did not seem to change and still fitted to a collapsed polymer coil with very similar Porod exponents. The wax was too large to fully resolve and was just observed as a surface. Low Q scatter was dominated by the wax and high Q values were dominated by the WASA. The WASA not significantly changing its shape in the presence wax suggests that it is present on the surface of the wax crystals rather than being incorporated into the bulk of the wax crystal as depicted in Figure 6.6.

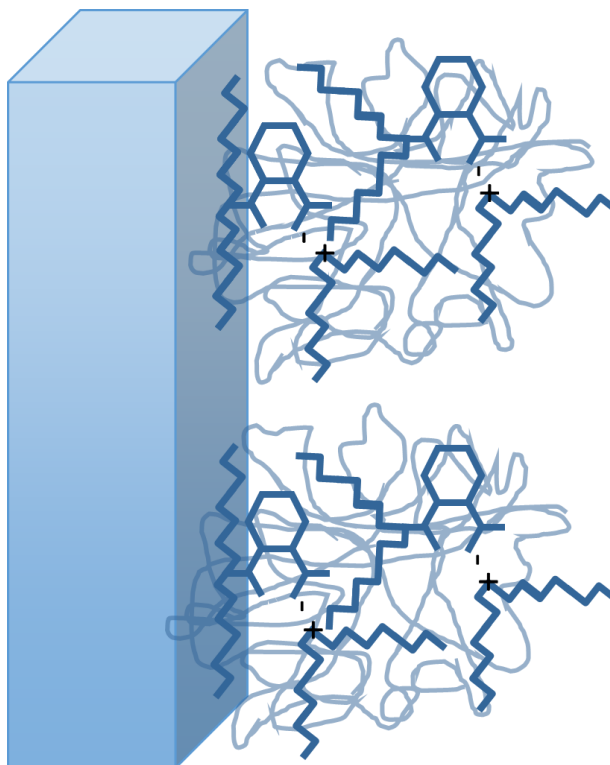


Figure 6.6: Schematic of the WASA as a collapsed polymer coil on the surface of the wax crystal.

6.3.3 SANS2D ISIS

ISIS allowed lower concentrations of WASA to be used and data was collected at a higher Q range. Lower concentrations of 0.1 wt% WASA still gave good scattering. Different concentrations of WASA in dodecane could all be fit to a binary mixture of hard spheres with hard sphere interactions at 15 and 25 °C. The smaller sphere was on average 14 Å in radius and the larger one 1200 Å. At 40 °C the larger sphere was not always seen. This could be due to the WASA being dissolved at higher temperatures and thus not forming the large agglomerated sphere.

A single WASA molecule has four 16 – 18 carbon length tails and an average carbon-carbon bond is 1.54 Å. Thus, it is rational to assume this 28 Å diameter sphere is due to a single WASA molecule. Subsequently the larger 2400 Å diameter sphere could be due to the combination of roughly 86 WASA molecules, as shown in Figure 6.7. This also agrees with the dynamic light scattering seen in Figure 5.11. The lower Q scattering which could not be fitted due to combinations of these larger spheres.

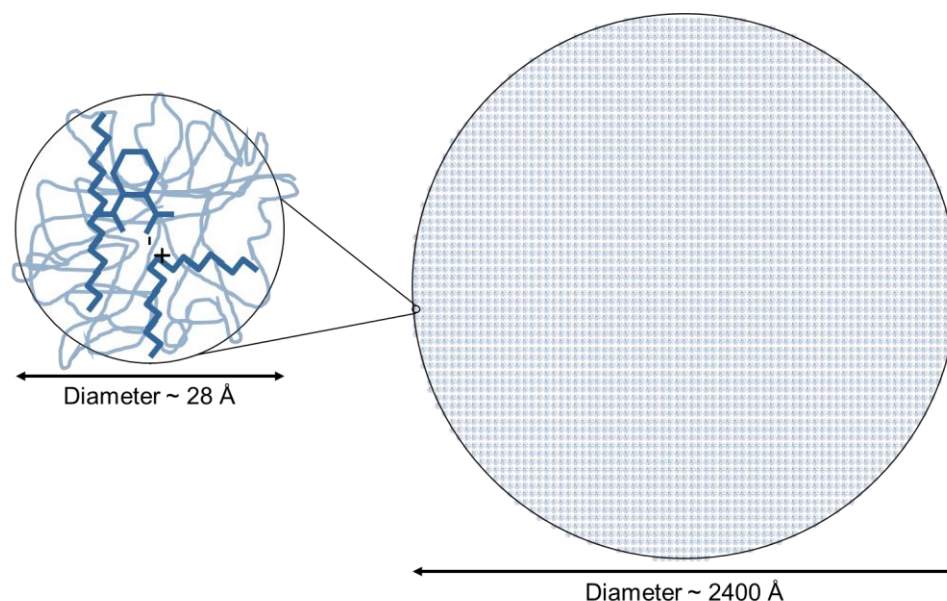


Figure 6.7: Schematic of the WASA binary sphere model.

In the presence of wax from the model diesel the WASA can still be fitted to a binary sphere model however the sizes are slightly different as shown in Table 6.1.

Table 6.1: Table showing the radii of WASA spheres fitting by the binary sphere model in different contrasts.

	H-WASA in D-Dodecane (Å)	H-WASA, D-wax in D-dodecane (Å)	H-WASA, H-wax in D-dodecane (Å)
Smaller sphere	14	17	9
Larger sphere	1200	801	781

Both the larger and smaller sphere radii decrease from H-WASA, D-wax in D-dodecane to H-WASA, H-wax in D-dodecane. The increase in WASA radius between WASA in dodecane and H-WASA, D-wax in D-dodecane could be due to several reasons. Firstly, the alkane chains on the WASA could have been forced to expand to co-crystallise with the wax crystal thus increasing the WASA sphere radius. Secondly, as the electrophoresis suggests, partial charge dissociation could have taken place with the anion preferably co-crystallising with the wax crystal and excluding the cation, thus making the distance between the ions larger.

The decrease in WASA radius between WASA in dodecane and H-WASA, H-wax in D-dodecane could be due to the H-wax masking the part of the WASA incorporated onto the wax crystal represented in Figure 6.8.

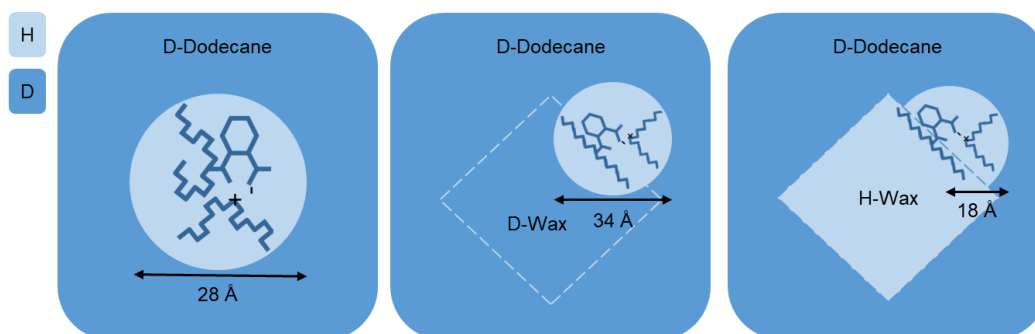


Figure 6.8: Schematic of smaller WASA spheres in the different contrasts.

The SANS2D data shows a difference in the WASA with and without the wax crystals. It is likely that this subtle difference was not detected in the NIST scattering because the sample was over saturated with WASA. 2.5 wt% WASA is the point at which the decrease in crystallisation temperature from DSC plateaus (shown in Figure 3.10). This suggests that there is excess WASA in solution, obscuring the scatter from the WASA on the wax surface.

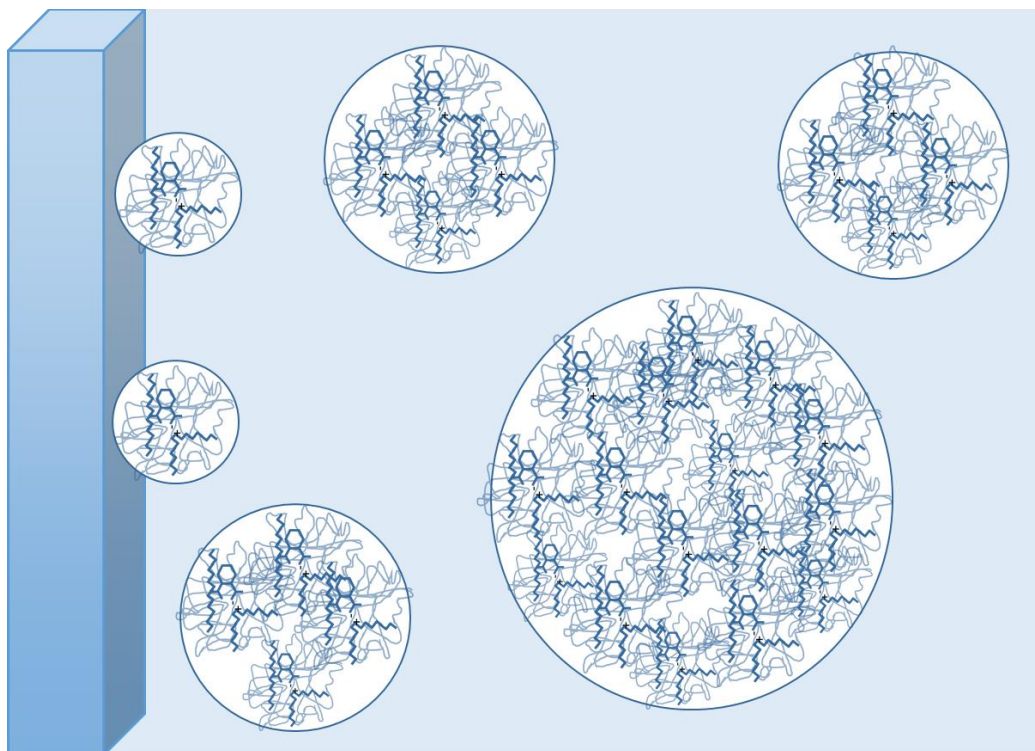


Figure 6.9: Schematic of excess WASA in solution obscuring the WASA on the surface of the wax crystal.

For comparison C₂₂ FVA was also run in the beamline. C₂₂ FVA in dodecane samples at 15 and 25 °C fitted nicely to lamellar phase model. Whereas, at 40 °C the large lamella structure is lost and the results fits to a cylinder model. The

lamellar phase could be a combination of these cylinders with either a single stretched C_{22} FVA polymer setting the lamella thickness or the side chains crystallising and forming lamella thickness with the more amorphous backbone lying between the layers as sketched in Figure 6.10.

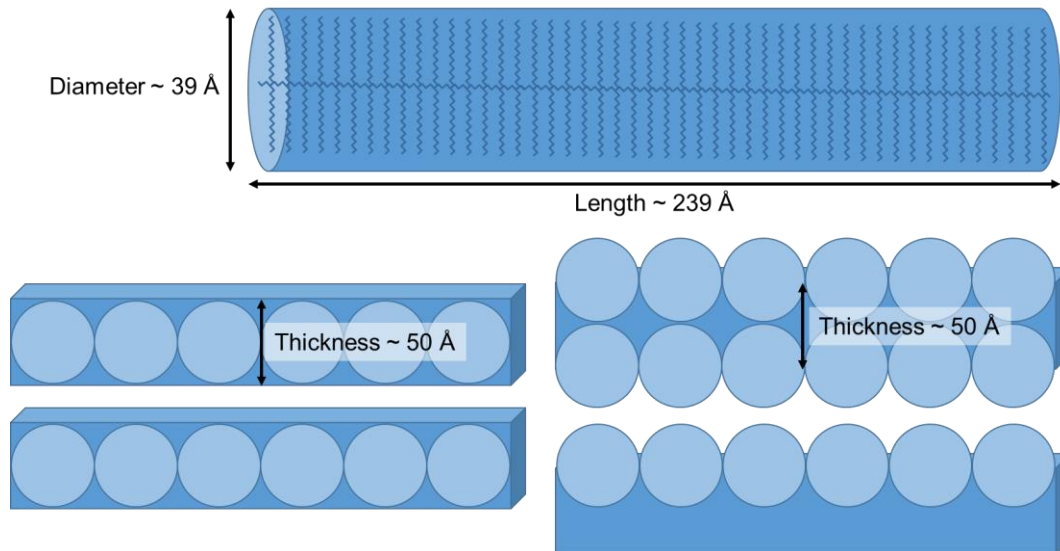


Figure 6.10: Schematic of C_{22} FVA as a cylinder and lamellar phase.

Upon addition of wax crystal in the model diesel the lamellar thickness is decreased dramatically to $44 \text{ \AA}$ for 0.5 wt% C_{22} FVA and only very weak scatter is shown for 0.1 wt% C_{22} FVA. This suggests that the C_{22} FVA is being incorporated fully into the wax crystal and losing its lamellar shape.

6.3.4 BT5 USANS NIST

The USANS data proved difficult to fit for the WASA doped model diesel. However, for the WASA only system it fitted well to a sphere model of radius $4.78 \text{ \mu m}$ this equates to 42 of the larger spheres agglomerations seen previously and 3320 single WASA spheres.

7 Conclusion and Future work

7.1 Conclusion

We can conclude several key findings on the position and mechanism of WASA. The WASA is incorporated onto the wax crystal reducing the wax crystal size and crystallisation temperature as shown by IR-spectroscopy and differential scanning calorimetry. XPS has shown that the WASA anion is more prominent on the surface of the wax crystal but was inconclusive about the cation. It suggests at on average at a depth of 56 Å (68 s etching time) only half of the original amount of WASA is present. This correlates with the SANS data suggesting that a single WASA molecule on the wax surface is 34 Å in diameter. The failure of other additives show that the molecular design of cold flow additives and their ability to incorporate into the wax crystal is crucial to their effectiveness.

Electrophoresis experiments show a positive charge present on the wax crystals due to the WASA, with the anion incorporated onto the wax and the cation less incorporated, creating a partial charge dissociation. The complex flows seen in the electrophoresis cell could be due to the high voltages causing the cation to be ripped off the wax crystal entirely leading to a negatively charged wax crystal. The WASA does not dissociate in the dodecane as shown by the conductivity testing. Adding organic salt to the system screened the charged wax crystals and reduced the attraction to the electrodes.

Rheological testing shows that the WASA causes a weak gel in the model diesel. The addition of the organic salt did not weaken the gel suggesting that simple electrostatics are not the main cause of the gelation

Small angle neutron scattering showed a single WASA molecule has a sphere of radius 14 Å. Single WASA molecules agglomerate into larger spheres with radii on the order of 1000 Å. The WASA has a collapsed polymer coil structure. This agrees with dynamic light scattering experiments. USANS showed further larger WASA spheres on the order of microns. In the presence of wax the WASA sphere increases in size to 17 Å. This is likely to be due to the anion WASA chains expanding and conforming to incorporate onto the wax crystal and to the partial

charge dissociation due to the cation not being incorporated onto the wax crystal as strongly.

The weak gel seen in the rheology is the mode by which wax anti-settling is achieved by the WASA. This shows that the WASA is actively causing the wax to gel and settle slower rather than simply reducing the wax crystal size and thus the settling speed. This implies a surface over a bulk effect. The mechanism of this weak gel can be theorised upon from the gathered results.

The many ways in which gels can form have been discussed in the introduction. A mechanical jamming of the wax crystals as seen in the un-doped model diesel can be ruled out due to the reduction in size and change in morphology of the wax crystals. The WASA increasing the viscosity of the dodecane can also be ruled out, as the WASA was shown to be on the wax crystal rather than in solution, and the piezo electric rheology showed no change with the WASA. The XPS shows that the anion is present on the surface of the wax crystal. The WASA causing an electrostatic gel was suggested by the electrophoresis. However, the weak gel was not destroyed by the addition of an organic salt which would have shielded the charges. The SANS showed that the single WASA molecules are roughly 28 Å in diameter which is maybe too small for the gel to be caused by purely by steric stabilisation.

We believe the mechanism of the WASA is due to the bridging interactions of cations between anions co-crystallised onto the surface of the wax crystal as sketched in Figure 7.1. The charges are not fully dissociated thus the organic salt cannot shield them and destroy the gel. Additionally, the long chains on the cations can contribute to stability *via* steric stabilisation.

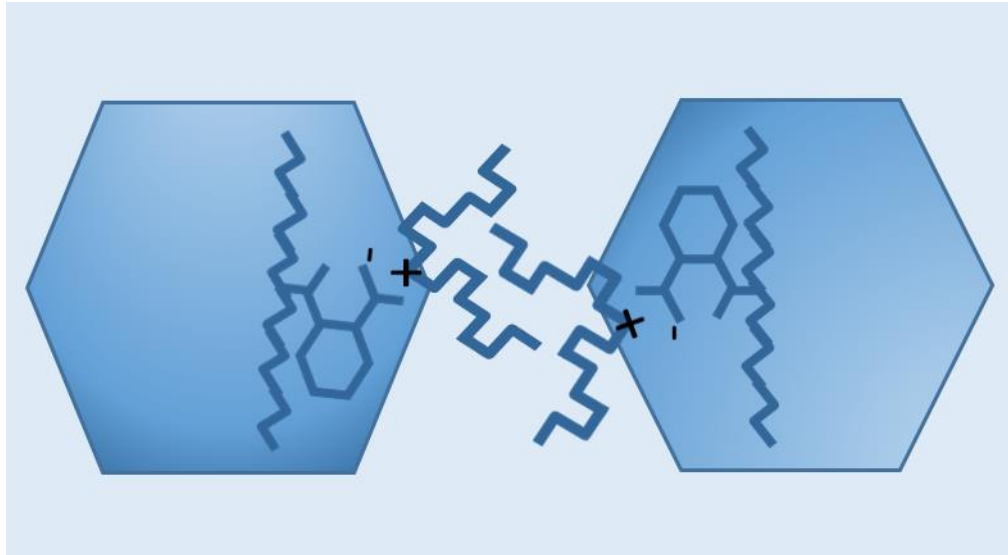


Figure 7.1: Schematic of cation bridging between anions co-crystallised with the wax crystals.

The aim of this work was to understand the mechanism of WASA and good progress has been achieved. The first positive experimental results that confirm the wax anti-settling phenomenon is caused by a weak gel is a major step forward in this area of research.

7.2 Future work

Future work would focus on verifying and testing our conclusions drawn with the currently available data.

7.2.1 Small angle neutron scattering

Further SANS work was proposed and accepted on D33 at ILL to help distinguish between the cation and anion of the WASA with and without the presence of the wax. However, due to the reactor problems at the ILL the beam run could not be scheduled before the end of the PhD. The partially deuterated WASA seen in Figure 2.5 could provide contrast between the cation and the anion as shown in Figure 7.2. The solubility of the deuterated WASA could be improved by using a toluene:dodecane or toluene:heptane solvent mix as WASA is more soluble in aromatic toluene. The location of the additives and amount of free additive within the system could also be explored using NMR diffusion techniques.

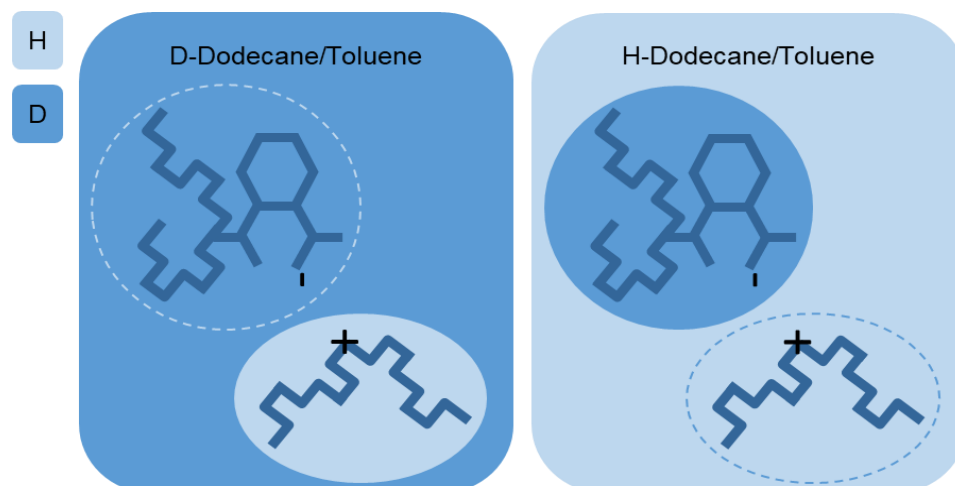


Figure 7.2: Schematic showing the contrast between WASA cation and anion.

7.2.2 Electrophoresis

Work has also begun on a smaller scale lower voltage electrophoresis cell. The cell is made by cutting and sealing together microscope slides and loaded with the model diesel *via* a syringe. The electrodes are platinum wires and the voltage box used has a maximum of 30 V. The distance between the ends of the electrodes can be varied and measured using a microscope. A schematic and photo of the prototype are shown in Figure 7.3. Using the microscope single wax crystals can be focused upon and tracked as the voltage is turned on. The current prototype has had problems with leaking and fragile joining sections.

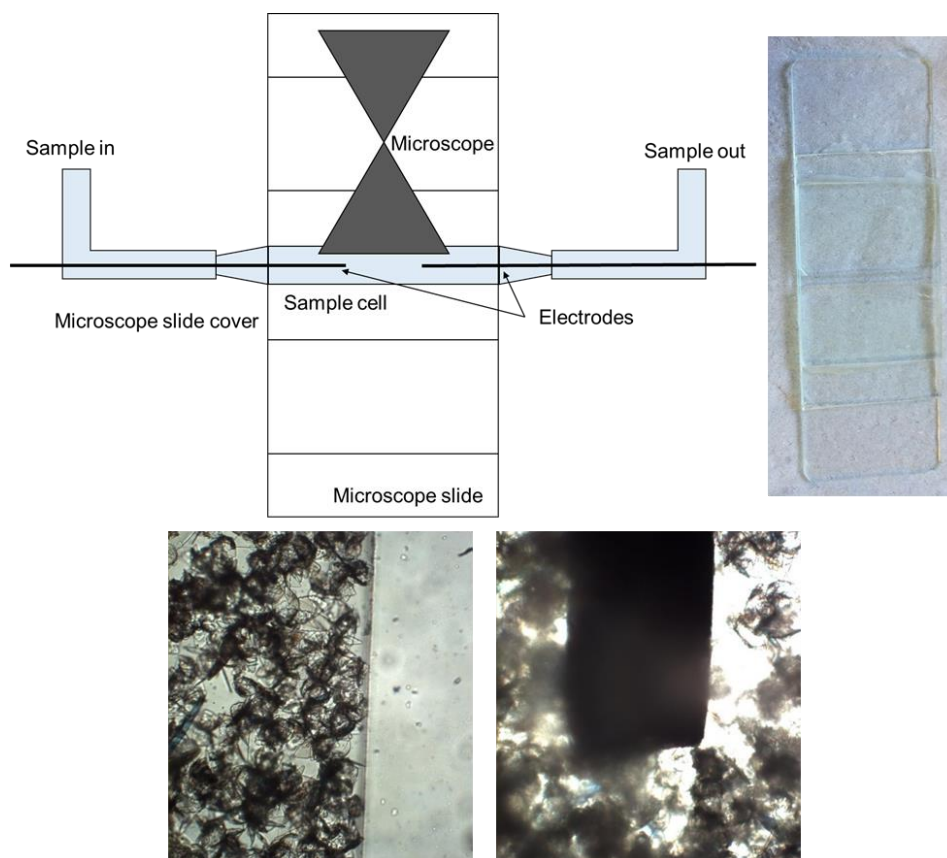


Figure 7.3: Top left: Schematic of lower voltage electrophoresis cell, top right: prototype of cell, bottom left: microscope image of wax crystals in cell and bottom right: microscope image of electrode.

Additionally, a more quantitative electrophoresis rig needs to be designed. The electrodes used could be modified to incorporate a non-conductive catchment area so the wax attracted to each electrode can be caught, weighed and tested. More Infineum commercial dispersants such as alkylphenol-formaldehyde condensate (HPFC) and PIBSA-PAM (polyisobutylene succinic anhydride backbones combined with polyamine) could be tried as these are thought to influence the stability of colloids in non-aqueous solutions. To measure the strength of the surface charge on the wax crystals an optical technique called phase-analysis light scattering (PALS) could be used as it is capable of measuring electrophoretic motilities of $10^{-12} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}$ allowing the use of lower voltages and detection of small surface charges, if the experiment can be done on micron sized particles.⁹⁸

7.2.3 Settling testing and crystal sizing

The MatLab code used to analysis the time lapse photography of the settling experiments and the experimental set up requires further development. Currently, the wax crystals are re-dispersed post crystallisation using a vortex mixer. This

may disrupt the weak gel. Experiments where the wax crystals are not re-dispersed post crystallisation also need to be conducted and the results compared. The thixotropy of the weak gel, caused by the WASA, could also be explored.

The effect of the size and shape of the container also needs to be investigated and eliminated. The preliminary settling experiments could also be improved by using a graduated cylinder to more easily measure the wax settling. The samples need to be left to crystallise in the cylinder before the settling test begins, so as to not disturb the gel.

An accurate and time effective way of measuring the wax crystal sizes needs to be developed. Use of the Morphologi G3 particle characterisation system from Malvern Instruments was attempted for this, however the contrast between the wax crystals and solution was not good enough. Polarising lenses could be used to improve the contrast along with writing a MatLab script to detect the wax crystals. Another solution could be the use of a Lasentec.

Conversely, repeatable wax settling tests could be done using a Turbiscan or making an apparatus mimicking that found in literature.¹⁰⁰ Ideally this equipment should also be able to measure the settling rate of the wax under slow cool conditions. Marie *et al.*⁴² used fast cooling conditions for their work, however fast cooling has been shown to affect the morphology of the crystal forming which could affect their settling rate.²²

Once the settling experiment, MatLab script and sizing of the wax crystals is complete, work needs to be conducted to fit this to a settling theory. This can then be used to help describe the wax crystal settling and its dependence on WASA.

7.2.4 Model diesel

The initial solvent used was dodecane due to its lower safety concerns, however this only models the aliphatic components of diesel not the alicyclic components. An 80:20 mix of heptane:toluene/xylene or kerosene could give different results. Changing the solvent to an aliphatic and aromatic mix also more closely resembles diesel. Repeating rheological, electrophoresis and settling experiments in different solvents and petroleum diesel will bring the model diesel closer to industrial application and allow screening techniques for new WASA molecules.

The cooling rate used to prepare samples is relatively quick and not controlled as the samples are small and are simply taken out the oven to cool to room temperature. Slow cooling rates are more representative of what happens to diesel in the field and are what many of the additives, including WASA, have been optimised for. Cooling rate also affects the size and morphology of the produced crystals. Slower cooling rates of around $1\text{ }^{\circ}\text{C min}^{-1}$ allow larger more regular crystals to grow and give closer representation to field settling. Consequently, different cooling rates need to be investigated.

7.2.5 Role of water

The role of water in the model diesel also needs to be thoroughly explored by using dried dodecane, doping it with increasing amounts of water and repeating the experiments. Further conductivity testing could also show the presence of reverse micelles.¹⁰¹

7.2.6 Full formulation

Diesel fuels are typically treated with a combination of EVAs, FVAs and WASAs along with other additives in a full formulation. The WASA should be tested in a full formulation the model diesel. It is known that additives may be needed to stabilise charges in solution. Commercial Infineum additive alkylphenol-formaldehyde condensate (APFC) has been suggested (Figure 7.4) as it is known to boost the activity of WASA without showing any cold-flow activity of its own.

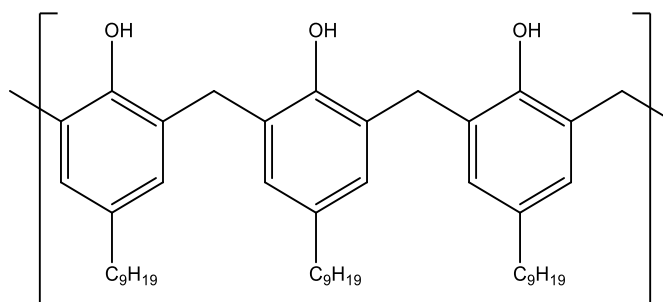


Figure 7.4: Alkylphenol-formaldehyde condensate, APFC (C9566).

It is not known how this boosts the WASA activity but specific structural features have shown to be important with hydrogen bonding and salt formation being suggested. Molecular modelling shows they have a calixarene ‘cup-like’ shape.⁴⁵

Combining what has been learnt about the mechanisms of these additives a better performing WAFI for diesel could be formulated. These further works studying the interactions of FVAs and WASAs should be investigated to build a full picture of how the additives interact with the wax crystal.

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