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Influence of wetting agent chemistry on associative interactions in hydrophobically modified cellulose ether systems

Master's Thesis in Materials Chemistry

AGNES TORPMAN

DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING

Division of Applied Chemistry

CHALMERS UNIVERSITY OF TECHNOLOGY

Gothenburg, Sweden 2026

www.chalmers.se

Abstract

Hydrophobically modified cellulose ethers are widely used as associative thickeners in water-based paints and their properties depend on the interactions with wetting agents and dispersed particles in the paint composition. These interactions are important for optimization of the composition with respect to viscosity, stability, and application. This project investigated two hydrophobically modified cellulose ether thickeners with different chemistry, hydrophobically modified ethyl hydroxyethyl cellulose (HM-EHEC) and hydrophobically modified methyl ethyl hydroxyethyl cellulose (HM-MEHEC), to explore the effect of methyl substitution on the polymer. The interactions with a number of nonionic surfactants were studied, and their structure and concentration were compared by measuring the rheological behavior, stability, particle size, and surface activity.

Rheological measurements of the viscosity demonstrated the dependence of both surfactant structure and methyl substitution on the polymer. Branched surfactants produced slightly higher viscosity than the linear ones, and a lower ethylene oxide (EO) content significantly increased it. HM-EHEC generally exhibited higher viscosity and the range was larger than for systems containing HM-MEHEC, indicating a weakened hydrophobic association with methyl substitution. The presence of propylene oxide (PO) groups shifted the viscosity maximum toward lower surfactant concentrations.

Stability was evaluated using backscattering (BS) measurements, with samples containing latex as well as the cellulose ether thickeners and surfactants. Phase separation was proven to increase with increased surfactant concentration, likely due to depletion flocculation. Dynamic light scattering (DLS) measurements supported the formation of larger aggregates at higher surfactant concentration, immediately after sample preparation. Over time, the method suggested adsorption of polymer-surfactant complexes onto the latex particles. Surface tension measurements also indicated complex dynamics of the polymer-surfactant systems since the results deviated from ideal critical association behavior, especially for surfactants with low critical micelle concentration (CMC).

Overall, the nonionic surfactants affected the associative behavior of the cellulose ethers differently and their structures affected the viscosity and surface tension of the systems. The choice of cellulose ether thickener, surfactant, and surfactant concentration is important to adjust for the application. The findings contribute to an improved understanding of the interactions between surfactants and polymers in waterborne paints and provide insights for future paint formulations.

Acknowledgements

This project has been enlightening and it has been fun to apply my knowledge from my studies on some ”real-world” problems.

I would like to thank everyone at Nouryon, that helped me with everything from instrument handling to tips for the presentation. It has been interesting learning from all of you and gaining an insight into what it is possible to work with within chemistry.

Especially, I would like to thank my supervisors at Nouryon, Helena and Sara, for helping me with all the methods, components, the report writing, and with some measurements when I have not been able to complete them on my own. I have learned a lot and it has been a great experience to perform all the laborations and help you further understand the interactions of your components.

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Contents

1 Introduction

Waterborne paints have gained increased prominence during the last decades due to environmental and health concerns with the previously dominating solvent-based paints [1]. Paints are important for creating an appearance that is both beautiful and energy-efficient in our homes, workplaces, and surrounding environment. The chemistry of the paints is consequently important in achieving desired performance and properties. Water-based paints face challenges because of the higher volatility compared to organic-based paints such as resistance to sags, runs, drips, good leveling, and ”open time” performance. The complex multicomponent formulations of these paints hinder their study. Solvents, binder, and additives, such as pigments, rheology modifiers, and wetting agents, interact in the formulation. All of these have varying chemistry and can be combined in different proportions. The combination of the components are crucial to formulate a paint with the desired properties both in the wet state, and on a dried, painted surface.

Nouryon produces both cellulose ether thickeners, that offer rheological control of paints, as well as wetting agents that give proper wetting, dispersion, and stabilization of paint components. The rheology of the cellulose ether thickeners affects the storage stability and application properties of the paint [1]. Wetting agents wet the surface of the incorporated particles and can affect the viscosity of the solution due to interactions with the cellulose ether thickener [1, 2].

Associative cellulose ether thickeners (HM-EHEC) are nonionic hydrophobically modified cellulose molecules that associate in solution, resulting in an increased viscosity [3]. Unmodified polymers in solution dramatically increase the viscosity as a result of the formation of an extended network when the polymeric chains entangle, as a consequence of increased concentration. Modified polymers additionally interact through the association of the hydrophobic side groups, similarly to the self-assembly of surfactants. The hydrophobic groups minimize the contact with water by forming physical bonds with each other and forming a water-poor domain between them. These bonds continuously break and reform, and the viscosity is significantly altered by the formed network. The substitution of certain groups will have an effect on the interaction. For example, these groups can be hydroxyethyl, ethyl, methyl, or larger hydrophobic groups.

Wetting agents are low molecular weight compounds that wet the surface of the paint components such as the pigments and binder [2]. They are typically surfactants, that adsorb at interfaces to lower the free energy of phase boundaries [4]. HM-EHEC interact

strongly with the surfactants in solution and form mixed micelles [3]. They start to interact at the critical association concentration (CAC) [5]. The increasing concentration of surfactant corresponds to an increase in the viscosity of the system, and the surfactants are incorporated in the self-associated hydrophobic groups of the polymer already at low concentrations [3]. The interactions between surfactant and polymer depend on the charge and structure of them. The presence of propylene oxide (PO) or amide groups can have an effect, but also hydrophobic chain branching or the ethylene oxide (EO) content, for example.

The interaction between the HM-EHEC and wetting agents depends on their respective chemistry. Therefore, it is relevant to study how the structure of these components affects the interaction. Due to the many structural variations and types of HM-EHEC and surfactants, many systems are yet to be studied. Rheological studies are necessary to study the viscosity and investigations of the surface tension variations to determine the CAC of the system. These methods help to understand the interaction between polymer and surfactant. For the paint application, it is also relevant to investigate the stability of the system when interacting with the binder. This can be done macroscopically by measuring the backscattering (BS), and at smaller length scales through dynamic light scattering (DLS) measurements.

1.1 Purpose

The thesis project focuses on gaining a deeper understanding of hydrophobic interactions between hydrophobically modified cellulose ether thickeners and nonionic wetting agents in the paint system and how these interactions are affected by the structure of these two components.

1.2 Objectives

The work investigates how various variables of the cellulose ether thickeners and the wetting agents influence the system by comparing two types of hydrophobically modified cellulose ether thickeners, HM-EHEC and HM-MEHEC, and five surfactants.

For the cellulose ether thickeners, the effect of methyl group substitution is studied by comparing a polymer with substituted methyl groups with one that lacks it.

For the wetting agents, the hydrophobic chain branching, EO content, and the presence of PO or amide groups are examined by comparing five surfactants that contain these groups.

The influence of these parameters is assessed by investigating properties including the viscosity and surface tension of polymer-surfactant systems. The stability of systems containing polymer, surfactant and latex is measured macroscopically using BS, and at lower length scales with DLS.

1.3 Limitations

During the project, two cellulose ether thickeners, five nonionic wetting agents, and one latex is used. This allows for a reasonable number of systems to compare and determine which parts of the components affect the behavior.

The cellulose ether thickeners that are studied are hydrophobically modified and limited to two. Effect of molecular weight and degree of substitution are not investigated.

The temperature behavior of cellulose ether thickeners and surfactants are not considered.

Pigment interactions are not included in the scope of this study.

2 Theory

Paints consists of numerous components that give them the desired properties. The composition of the paint varies, depending on the type of paint. Typically, a paint consists mainly of 20-50 wt% pigments, 20-50 wt% binder, 10-30 wt% solvent and 5-20 wt% additives (such as thickeners and surfactants) [6]. Other components in smaller amounts are extenders, retarders, driers, fragrances and preservatives.

In this study, the components studied are additives, thickeners and surfactants, and latex binder. The behavior of the individual components in aqueous solution is presented as well as the interaction between them. The principles behind the characterization methods are also presented.

2.1 Cellulose ether thickeners

The cellulose ether thickeners studied in this project are those with the trade name Bermocoll®, which are provided by Nouryon. These are water-soluble, nonionic and are based on cellulose from wood pulp or cotton linters [7]. They are mostly used in water-based paints and building products, but have many other industrial applications. The Bermocolls are produced with different types of chemistry: ethyl hydroxyethyl cellulose (EHEC), methyl ethyl hydroxyethyl cellulose (MEHEC) and hydrophobically modified (methyl) ethyl hydroxyethyl cellulose (HM-(M)EHEC). Thickeners of the type HM-(M)EHEC are relevant to this study to investigate the hydrophobic interactions with different wetting agents.

Cellulose is a polysaccharide and is not water soluble, but it can be chemically modified to achieve water solubility [3]. This starts with an activation of the molecule through alkalization followed by modification by reaction with ethylene oxide (EO) and then ethyl- and methyl-chloride [8]. The modification is done on the 1.4-anhydroglucose unit (AHG) in the polysaccharide, and specifically on the hydroxyl groups [3]. A chain growth reaction is also happening since the modification reactions generates new hydroxyl groups, which results in the formation of short EO groups. The molar substitution of EO (MS_{EO}) is the average number of EO units on the AHG. Addition of long chained alkyl groups to this structure would result in a HM-MEHEC and an example of this type of structure is presented in Figure 2.1.

There are additional substitution parameters used to describe the modification of the molecule, useful for the chemical characterization and understanding of the interactions between the cellulose ether thickeners and the wetting agents. The degree of substitution (*DS*) is the number of hydroxy groups per AHG that have reacted and can be a number

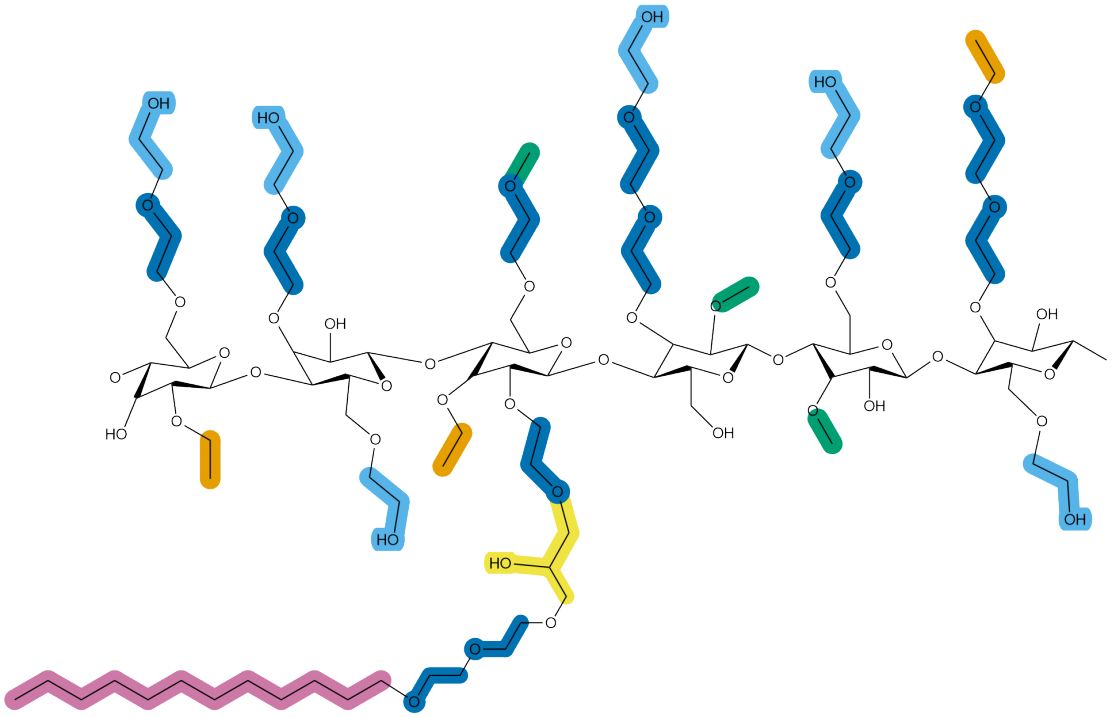


Figure 2.1: Representative molecular structure of a Bermocoll HM-MEHEC. The blue groups represent hydroxyethyl groups where the dark blue represents hydroxyethyl groups that have reacted further, and the light blue the end-group. The orange exemplifies ethyl groups and the green methyl groups. The pink is an example of a hydrophobic group. An HM-EHEC has a similar structure but has a lower substitution of methyl groups.

between 0 and 3 [3]. DS_{ethyl}, DS_{methyl} and MS_{EO} are average values of the substituted groups. The numbers are not exact since the substitution is not a perfectly homogeneous distribution.

When alone, the thickening mechanism of the cellulose ether thickener is mainly based on entanglements of the polymeric chains and associations between hydrophobic parts of the molecule [3]. This effect is increased with an increase in polymeric concentration where the polymer chains interact more strongly, start to entangle, and form a transient network. This results in a dramatic increase of the viscosity, from that of pure water. This will be further described in Section 2.4 and demonstrated in Figure 2.5. However, hydrophobic interactions also contribute to the thickening effect. The hydrophobic groups on the AHG units associate in aqueous solution, similarly to the self-assembly of surfactants into micelles, where they bond physically. These non-covalent bonds break and reform continuously since they are reversible. The interactions are influenced by the length of the hydrophobic groups, the molar substitution, and the distribution of the groups. The strength of the hydrophobic interactions are affected by these components.

The viscosity of a polymer solution can be influenced by the addition of a salt with the effect being either an increase or decrease, depending on the nature of the salt. These

effects are more pronounced for the hydrophobically modified polymers than for their unmodified counterparts [9]. With the addition of a salt with a small anion (e.g. NaCl), the viscosity increases because of the elevated surface energy, which raises the energy barrier required to break the physical bond between the hydrophobic chains. Conversely, the addition of a salt with a large anion (e.g. NaSCN) results in the opposite effect, since the anion competes for and occupies the hydrophobic domains within the network, weakening those interactions. Overall, the presence of salt is expected to have an impact on the viscosity of a polymer solution.

The solubility of polymers, and thus the viscosity of the solutions, are also dependent on temperature, but this will not be investigated in this study [9].

2.2 Wetting agents

To ensure proper dispersion of the components in the paint, a wetting agent is required. This improves the interaction between the dispersed and continuous phases by lowering the interfacial tension and wetting the surfaces of the included pigments and fillers [2]. This is possible through their surfactant structure, consisting of a hydrophilic head group and a hydrophobic tail, that allows them to orient at interfaces and mediate compatibility between otherwise immiscible phases [10]. The hydrophobic tail commonly consists of a long hydrocarbon chain, which makes it insoluble in water and thus orients itself towards the nonpolar phase. Since the polar head behaves oppositely, the orientation of these amphiphilic molecules reduces the surface tension and improves the dispersion between the two phases.

When surfactants are added to water, they immediately occupy the interface between water and air to minimize the surface free energy [11]. When the surfactant concentration increases and the interface is saturated, the critical micelle concentration (CMC) is reached. This is the concentration at which the amphiphiles start to aggregate into clusters called micelles. These are generally spherical structures where the surfactant tails are oriented inward and the heads outward, towards the polar solvent, minimizing the contact between the hydrophobic parts and the surrounding solvent. The size of the micelles are usually 5-100 monomers in length [12]. At concentrations above the CMC, the surface tension will be constant since the surfactants will go into micelles instead of the interfaces [11]. A schematic plot of the surface tension behavior of surfactant solutions is illustrated in Figure 2.2. This behavior makes the CMC an important parameter because it provides information on how much the surface tension of a solution can be lowered [13]. In the formation of a paint, it is relevant to use an amount of wetting agent that improves wetting, spreading, and adhesion of the various components in the

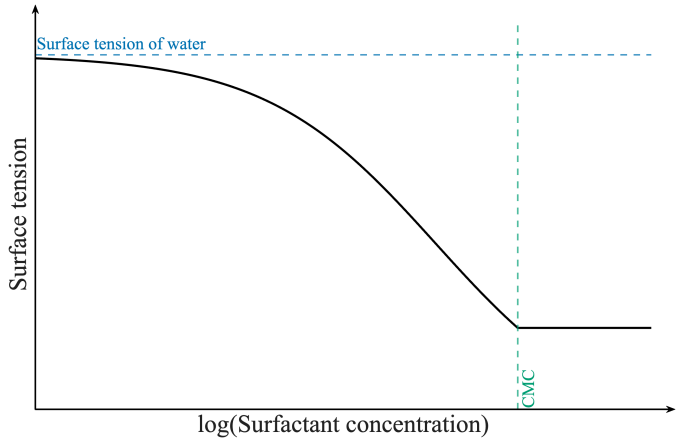


Figure 2.2: Schematic plot of the surface tension depending on the surfactant concentration in aqueous solution. Inspired by [5].

composition and of the paint itself. In this study, nonionic wetting agents are used and their low CMC values make them useful especially at low concentration [12].

Wetting agents also contribute to stabilization through two main mechanisms: electrostatic and steric stabilization. Electrostatic stabilization relies on the ionic charges on the dispersed particles [2]. The DLVO theory, developed by Boris Derjaguin, Lev Landau, Evert Vervey and Theodoor Overbeek, and illustrated in Figure 2.3, is based on this and functions through the repulsion of particles due to their same electrical charge [14]. It suggests that the sum of attractive van der Waals forces and repulsive double layer interactions results in the total interaction energy between colloidal particles. As Figure 2.3 shows, there is an energy barrier at short distances, where the van der Waals forces dominate and there is a state of stable attraction. The passing of this energy barrier results in a, potentially irreversible, aggregation or coalescence of particles. A primary maximum arises at intermediate distances because of the electrostatic repulsion when electric double layers overlap. The formed energy layer can prevent aggregation. When increasing the distance, there is a secondary minimum where van der Waals forces compete with the electrostatic repulsion, resulting in a small energy minimum. Electrostatic repulsion diminishes with increasing distance, and the potential energy decreases gradually due to the domination of van der Waals attraction. As can be interpreted, the colloidal stability is determined by the balance between the attractive van der Waals forces and the electrostatic repulsion. The degree to which electrostatic stabilization is possible can be measured through the zeta-potential of the particle [2].

The second stabilization mechanism, steric stabilization, relies on adsorbed surfactant molecules or polymer chains on the particle surface [2]. The particles are separated due to a decreased configurational entropy with an increased polymer concentration as the

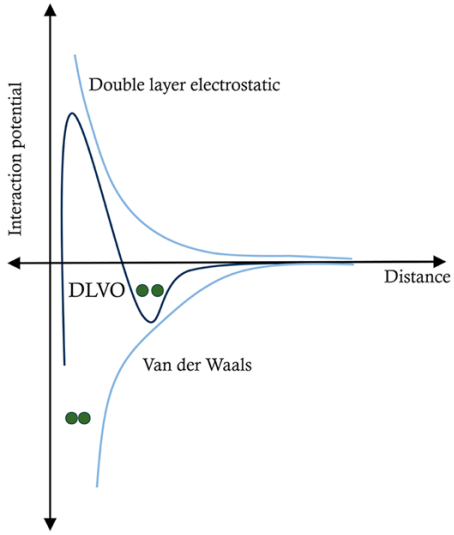


Figure 2.3: The potential energy for colloidal systems. Retrieved from [14].

particles get closer together, leading to an osmotic flow that separates the particles and prevents particle aggregation. Steric stabilization is the more important mechanism in this study because of the use of nonionic surfactants.

Wetting agents are also relevant for maintaining the desired viscosity of the paint formulation [2]. This is further explained in Section 2.4 where its dependence on the interaction with the polymer is considered.

Since nonionic surfactants are uncharged, they have low sensitivity to electrolytes and pH [12]. They also have an inverse solubility behavior, where an increased temperature results in a decreased solubility. However, the temperature dependence will not be investigated in this study.

One of the most important types of nonionic surfactants are alcohol ethoxylates [15]. Their hydrophilic part consists of repeating units of EO with a hydroxyl group at the end, and their hydrophilic tail consists of an alkyl chain. The monomers will have different lengths from the production of the surfactant resulting in a chain length distribution. Alcohol alkoxylates have repeating EO, and also PO units in the hydrophilic part of the molecule [16]. Fatty alkyl amide ethoxylates are similar to the ethoxylates but also contain an amide group in the head group [17]. It has been shown that the presence of this group can lead to a decrease in CMC and an increase in surface tension at this concentration, which probably depends on the formation of hydrogen bonds between the molecules and the increased size of the polar head group. Structures of the surfactant relevant to the study are presented in the Materials section (3.1) in Figure 3.1.

The solubility in water of ethoxylated surfactants is high because of hydration of the

hydroxyl groups, but is also dependent on the amount of EO and the length of the alcohol alkyl group [12]. The solubility increases with more EO groups and a smaller alkyl group.

The branching of the hydrophobic part of the surfactant affects the surfactant behavior, and branched alkyl surfactants are typically less efficient than linear ones [18]. This depends on the bulkier structure, which results in a less efficient packing of the surfactants at the interfaces and in the micelles. An increased chain length usually results in a decreased CMC [12].

2.3 Binder

A binder works as the glue of the paint formulation by holding pigments together and adhering them to the surface [19]. Adhesion, flexibility and durability are also provided by its film-forming properties. In this study, an all acrylic latex is used, which is a polymer based on acrylic acid, methacrylic acid, and its esters [20]. Latexes offer UV-resistance and protection against cracking and blistering in the paint formulation.

Latexes are polymer colloids, usually with a milky appearance, and the particles are generally spherical [21]. Surfactants are used as stabilizers in the formulation and as the reactants in the production of the solid latex particles. The stabilization is required to minimize the effect of Brownian motion and attractive van der Waals forces. The main alternatives to stabilization of the system are steric and electrostatic stabilization, described in the previous section (2.2).

To obtain a latex with the desired physical properties, it is necessary to use two to three polymers for the copolymer [22]. In the latex used, these are acrylic acid, methacrylic acid, and its esters, as mentioned above. A combination of polymers could for example change the minimum film forming temperature (MFFT) of the latex, give an increased viscosity, or improved wet adhesion.

2.4 Interaction between polymers, surfactants and latex

The concentration at which surfactant and polymer start to interact is called the critical association concentration (CAC) [5]. It indicates a strong co-operative binding and can be determined by studying the surface tension of the system with increased surfactant concentration. This is demonstrated in Figure 2.4. When surfactant first is added, the surface tension will most likely be constant, but it depends on the surface activity of the polymer. When the surface tension decreases, it indicates an increased surfactant activity. When the surface tension becomes constant, the CAC is reached. At this

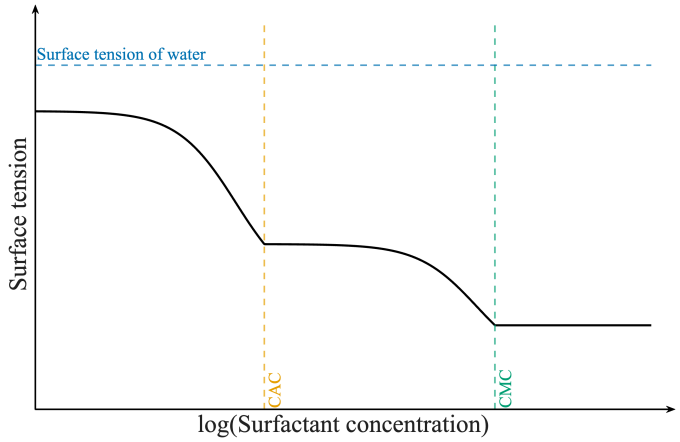


Figure 2.4: Schematic plot of the variation in surface tension depending on the surfactant concentration in solutions containing polymer and surfactant. Adapted from [5].

concentration, there is no further lowering of the surface tension because of no further increase in surfactant adsorption at the air-water interface. Eventually, the polymer is saturated with surfactant, which again will lead to an increased surfactant activity and a further reduction of the surface tension, until the CMC of the surfactant is reached. As previously described, the surface tension is then constant and regular micelles start to form.

The CAC is usually lower than the CMC of the surfactant [23]. For nonionic surfactants, the CAC is usually close to the CMC because of the hydrophobic interactions with nonionic polymers. In this study, the CAC is investigated by measuring the surface tension.

There are two main models describing the interaction between polymer and surfactants in solution [5]. The model relevant for the studied systems in this report is the one describing the system as strongly co-operative through association between the two components. The cause of is the hydrophobically modified polymer, which is an amphiphilic molecule that interacts by hydrophobic interaction and self-associates, similar to surfactants. This is illustrated in Figure 2.5. These interactions result in an increased viscosity, which makes these polymers useful as rheology modifiers in paints. Addition of surfactant results in a further viscosity increase, because of increased relaxation times [3]. This is a consequence of the strong association between the hydrophobic groups of the polymers and surfactants, and corresponds to a peak in viscosity which usually appears in the proximity of the CAC [5]. However, at higher surfactant concentrations, the increased viscosity effect is lost because there is not a sufficient amount of hydrophobe in each micelle, leading to the loss of connectivity in the physical network. This results in a decrease in viscosity due to the absence of

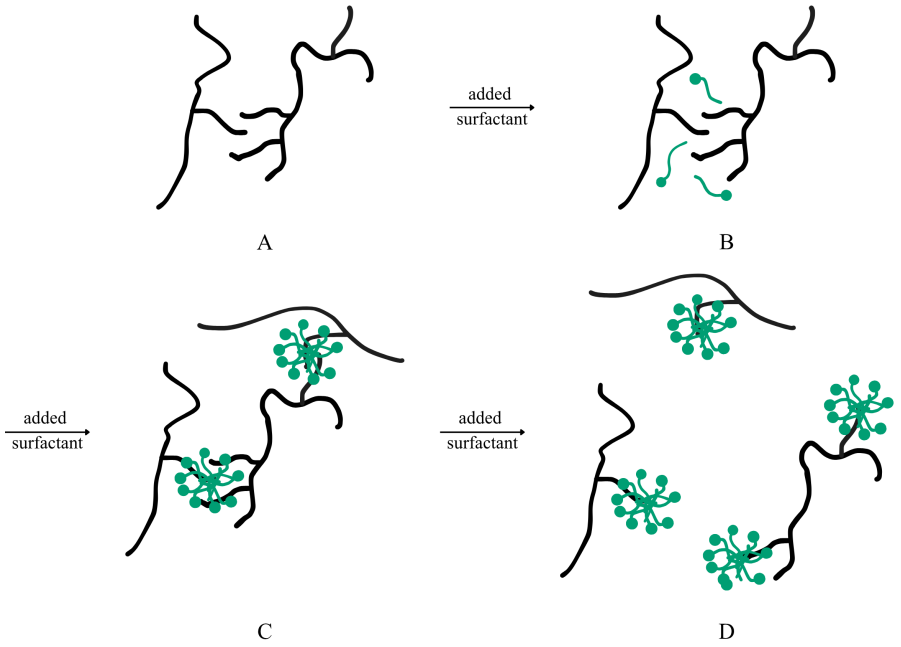


Figure 2.5: The self-association of HM-(M)EHEC and surfactant with increasing surfactant concentration, adapted from [5]. The black structures are the HM-(M)EHEC and the green are surfactants. In A, there is a weak aggregation between the hydrophobic groups on the polymers. Between B and C, the cross-links between the polymer chains are reinforced by the increased surfactant concentration. D shows the loss off cross-links at high surfactant concentration.

cross-links. The substitution of methyl on the HM-(M)EHEC is therefore relevant to consider when studying the viscosity. This viscosity behavior is illustrated in Figure 2.6.

When latex is added to the polymer-surfactant solution, the behavior is further altered. At low surfactant concentrations, the polymer-surfactant complexes adsorb to the latex particle [24]. Hydrophobic interactions between adsorbed polymers allow for the aggregation of these latex-polymer-surfactant structures through bridging flocculation.

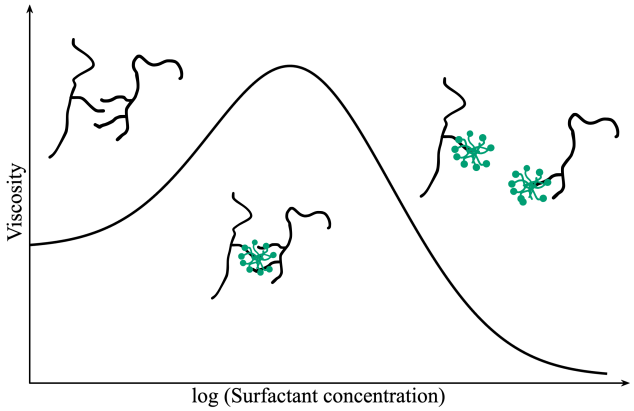
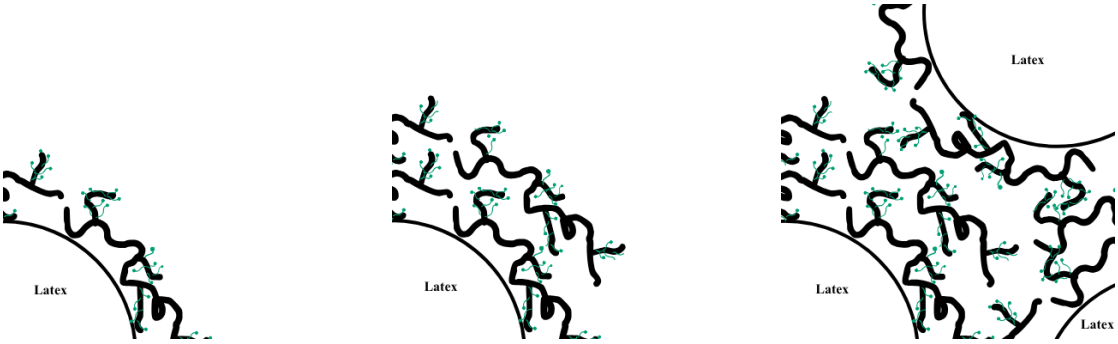


Figure 2.6: Viscosity dependence on surfactant concentration and the extension of a polymer network, adapted from [3].



(a) Polymer-surfactant complexes adsorbed to the latex particle.

(b) Aggregation of polymer-surfactant structures on the surface of the latex particle.

(c) Aggregation of latex-polymer-surfactant complexes through bridge formation.

Figure 2.7: The aggregation behavior of latex-polymer-surfactant systems by bridging flocculation. Adapted from [24].

The aggregation is illustrated in Figure 2.7. With an increased polymer concentration, the network becomes more uniform, and the particle dispersion as well [25]. The thickening effect leads to a severe decrease of Brownian motion and can be increased with an addition of polymer, surfactant, or both. This bridging flocculation is desired for the required coating properties of the paint. The interactions are between hydrophobic side groups that are not physically bound with surfactant or latex [24]. Interactions have shown to be restricted to a limited concentration (2-4 mmol/kg in one study [24]) and thus it can be assumed that the hydrophobic interaction between polymer and surfactant governs this flocculation. Similarly to the previously described polymer-surfactant behavior, the polymers have been observed to desorb from the latex at higher surfactant concentration, where depletion flocculation occurs [24, 25]. This also indicates a poor dispersion with reduced physical and optical properties [25]. Depletion flocculation is more common in paints than bridging flocculation, but bridging flocculation generally is a stronger interaction. However, compared to depletion flocculation it is more difficult to break up with mechanical energy and reforms faster.

2.5 Characterization methods

Multiple methods are used to characterize the systems in this study, and their principles are presented below.

2.5.1 Rotational rheometry

Rheological measurements are performed to determine the viscosity dependence on surfactant concentration and to investigate the CAC of the systems.

Rheology is the study of flow and deformation and is important when studying the components of paints since these have a complex rheological behavior [26]. There are various types of rheological measurements such as viscosity, yield stress, creep, and zero-shear viscosity [27]. These are important to study the behavior of the paint in the numerous situations it is exposed to, all the way from sitting in the can to being applied to the surface. Some shear rates to consider for paint applications are the leveling due to surface tension (10^{-2}-10^{-1} s^{-1}), draining under gravity (10^{-1}-10^{1} s^{-1}), the "in-can-viscosity" when stirring the paint (10^{1}-10^{3} s^{-1}), and application by spraying or brushing (10^{3}-10^{4} s^{-1}) [26].

For Newtonian liquids, the viscosity is independent of the shear rate and the viscosity is constant [26]. Paint is a non-Newtonian material and therefore behaves nonlinearly and the viscosity varies with the shear rate. Figure 2.8 illustrates the typical behavior for a non-Newtonian liquid in a flow curve.

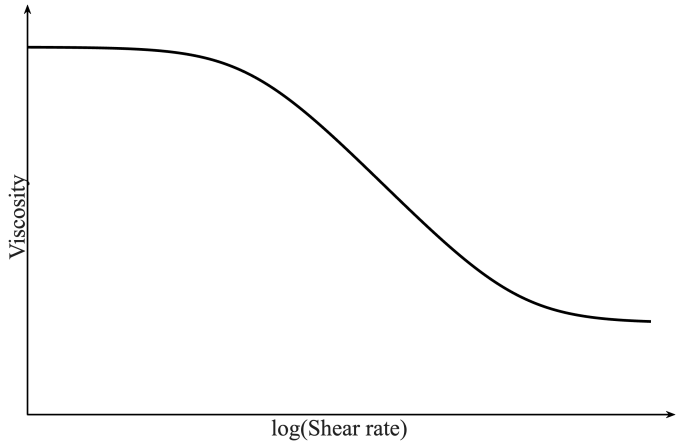


Figure 2.8: Flow curve of a typical non-Newtonian liquid describing the shear rate dependence of the viscosity. Redrawn from [28].

The rheological studies in this work are done with the cone and plate measurement geometry. This provides a system where the shear rate and shear stress are constant throughout the sample and the temperature rise is minimized [29].

2.5.2 Du Noüy ring tensiometry

Measurements of surface tension are performed to investigate the CAC of the polymer-surfactant systems, which is dependent on the surfactant concentration and is described in Section 2.2.

The surface tension is measured using the Du Noüy ring method where the force acting on a ring, that is withdrawn from a liquid, is measured [30]. An illustration of the method is provided in Figure 2.9. When the lamella, produced when the ring passes the phase

boundary, aligns vertically with the plane of the ring, a force maximum arises. This force (F) correlates to the surface tension (σ) according to Equation 1.

$$\sigma = \frac{F}{L \cdot \cos\theta} \tag{1}$$

L is the wetted length of the ring and θ is the contact angle between the receding ring and the liquid. Generally, it is assumed to be 0° for liquids because of the optimal wettability of the standard platinum-iridium ring used, resulting in $\cos\theta = 1$. A correction is required to consider that the weight of the lamella increases the measured force, and is included in the instrument. The measured surface tension might not reflect the true equilibrium, since the adsorption of molecules at the interface is a dynamic process. However, it is quasi-static - additions are made slowly with stabilization in between - the surface tension might not be fully equilibrated before each measurement. This is especially true at low surfactant concentrations where the adsorption kinetics are slower.

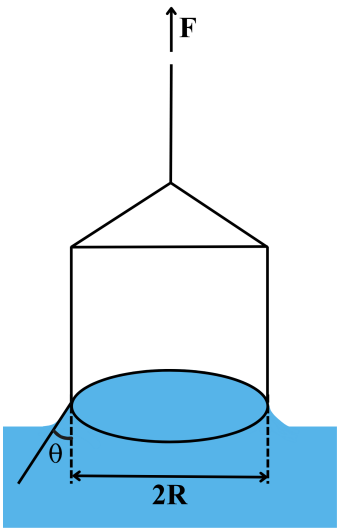


Figure 2.9: Schematic representation of Du Noüy ring tensiometry including the contact angle (θ), the force (F) and the radius of the ring (R). Inspired by [31].

2.5.3 Static multiple light scattering (SMLS)

Sample stability is detected using static multiple light scattering (SMLS) and the backscattering (BS) signals are recorded as a function of sample height. These are based on multiple light scattering, which is the phenomenon in which photons scattered by the sample are rescattered from neighboring atoms before reaching the detector [32]. BS is useful for detecting the uniformity of a sample over time, which makes it useful for studying the stability of colloidal dispersions, such as paint [33]. Specifically, coalescence, flocculation, creaming, and sedimentation can be monitored.

2.5.4 Dynamic light scattering (DLS)

Dynamic light scattering (DLS) is a technique used to determine the size of particles dispersed in a liquid [34]. These are typically in the sub-micron region but can also include macromolecules. The sizes of the particles are determined by measuring the intensity variations of the scattered light. The rate at which this intensity fluctuates is connected to the Brownian motion of the particles via the so-called correlation function. Smaller particles cause a more rapid fluctuation of the intensities due to the constant motion of the particles leading to a more rapid change in the interference. The velocity of the Brownian motion is represented as the translational diffusion coefficient (*D*), which can be calculated from the correlation function. *D* can be used to calculate the size of a particle via the Stokes-Einstein equation, presented in Equation 2.

$$d_H = \frac{kT}{3\pi\eta D} \tag{2}$$

From this equation, it is clear that the temperature (T) and viscosity (η) are important for these measurements. k is the Boltzmann constant, and d_H is the hydrodynamic diameter corresponding to a sphere with that same D. Also, multiple light scattering has to be minimized to obtain the most accurate results and therefore, the samples have to be dilute [32]. Multiple light scattering minimizes the randomness of the scattering signal, making it appear so that the particles are moving faster than they are.

Another important aspect of these measurements is the choice of the refractive index (n) of the dispersant, which is used to calculate D. Because of the four components in the measured system (surfactant, polymer, latex and water), n and η of the polymer and surfactant in solution should also be considered. Since n for both components is close to that of pure water (1.33), the n of water is used.

3 Experimental

3.1 Materials

The materials used in this study are mainly manufactured by Nouryon and are confidential. Thus, other names are provided with simplified structures and other parameters necessary for the analysis of the studied systems.

3.1.1 Cellulose ether thickeners

The two cellulose ether thickeners are used as the polymers of the systems, both of them are hydrophobically modified, one is an HM-EHEC and the other an HM-MEHEC. Both are types of Bermocoll®, supplied by Nouryon.

The relevant properties for the two polymers are presented in Table 3.1. It can be observed that the differences between these two polymers are MS_{EO}, DS_{ethyl}, and DS_{methyl}, since $MS_{hydrophobe}$ and the molecular weights are the same. However, the most prominent feature is the substitution of methyl. Both contain about 5 wt% salt.

It is relevant to know that Bermocoll® requires the addition of a base for proper dissolution [35]. It should be added to water that is neutral or slightly acidic since it forms an insoluble gel if added to an alkaline solution because of too fast dissolving. The pH should be between 8 and 9.

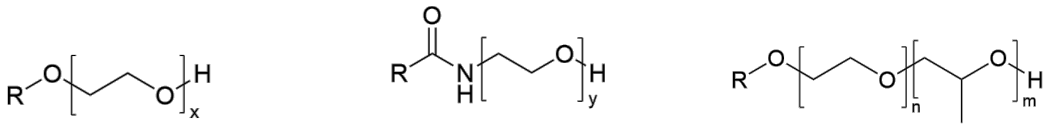
Table 3.1: Characteristics of the cellulose ether thickeners.

	Hydrophobe	MW (g/mol)	$MS_{hydrophobe}$	MS_{EO}	DS_{ethyl}	DS_{methyl}
HM-EHEC	C_{12}-C_{14}	200,000	0.005-0.01	2.2-2.5	0.9-1.0	0.05
HM-MEHEC	C_{12}-C_{14}	200,000	0.005-0.01	1.5-1.8	0.2-0.3	0.5-0.7

3.1.2 Wetting agents

The wetting agents will be mentioned as the surfactants of the system. All of them are provided by Nouryon and will be presented with other names than their commercial ones.

In Table 3.2, the names and relevant parameters are presented for the surfactants investigated. The names are constructed by referring to the structures of the surfactants. The chain of the hydrophobic tail is linear or branched and is shown with ”LC” and ”BC”, respectively. ”EO”, ”AO” and ”AMEO” represent ethylene oxide units, alkoxylate units, and alkyl amide ethoxylate units in the polar head of the surfactants. These structures are presented in Figure 3.1. The type of branching is not presented in the BC surfactants



(a) Alcohol ethoxylate. **(b)** Fatty alkyl amide ethoxylate. **(c)** Alcohol alkoxylate.

Figure 3.1: The structures of the studied surfactants. a) *R* is a branched C_{10} chain for both BC10EO8 and BC10EO5, and *x* is 8 and 5, respectively. For LC(12-16)EO8, *R* is linear with a mixture of chain lengths (C_{12}-C_{16}) and *x*=8. b) *R* is a linear C_{12} chain and *y*=8. c) *R* is a mixture of chain lengths of C_{10}-C_{16} for LC(10-16)AO10 and *n*>0 and *m*>0.

Table 3.2: Characteristics of the surfactants.

Surfactant	Description	CMC (mM)
BC10EO8	C_{10} alcohol ethoxylate	3.17
BC10EO5	C_{10} alcohol ethoxylate	2.88
LC(10-16)AO10	C_{10}-C_{16} alcohol alkoxylate	0.13
LC(12-16)EO8	C_{12}-C_{16} alkohol ethoxylate	0.02
LC12AMEO8	C_{12} fatty alkyl amide ethoxylate	0.04

since the products are confidential. LC(10-16)AO10 is also confidential and consists of structures with various chain lengths (C_{10}-C_{16}). The exact number of EO and PO units will not be presented. LC(12-16)EO8 also has a chain length distribution (C_{12}-C_{16}).

3.1.3 Binder

The latex used in this work is Mowilith® LDM 7717 (Celanese, Dallas, TX, USA), which is a pure acrylic binder with low water uptake and good hardness [36]. It is an aqueous copolymer dispersion with a particle size of 0.12 μm and consists of 46 % solids with the stabilization system consisting of surfactants [36, 37].

3.2 Methodology

3.2.1 Sample preparation

For each measurement, samples were prepared in a similar way but with varying concentrations. All samples included polymer and surfactant, latex was also included for SMLS and DLS measurements. The variation in concentration of the polymer was chosen depending on the method used and the viscosity that was best suited for the method. For example, a higher concentration was used for the rheological measurements than for surface tension measurements.

When the samples were prepared, two stock solutions were created. One included only polymer, and the other both polymer and surfactant. These solutions were then mixed

into the desired concentrations for the measurements. All concentrations are reported by weight.

For the stock solution containing surfactant, the surfactant was weighed first followed by water. The polymer was then added carefully when this solution was stirring on a magnetic stirrer. When it had dispersed throughout the solution, a drop of the base 2-amino-2-methyl-1-propanol (AMP-90™) was added per 100 g of solution, to fully dissolve the polymer. The solutions were left on the stirrer for a few hours to ensure complete dissolution. The samples for each measurement were then prepared by first adding the desired amount of surfactant solution, followed by the polymer solution. For the dispersions containing latex, this was added as a final step with a dry concentration corresponding to 20 wt%.

3.2.2 Purification of the cellulose ether thickeners

The cellulose ether thickeners have the form of a free-flowing powder and include some unreacted hydrophobe, and other acetone soluble materials that might affect the interactions in solution. To remove these interactions, the cellulose ethers can be washed. 30 g of the cellulose ether powder was dispersed in 100 ml of 99 % acetone and put on a magnetic stirrer for 15 minutes. Subsequently, the dispersion was vacuum dried using a Büchner funnel and a filter paper. These steps were repeated two times with 99.8 % acetone. Finally, the powder was left to air dry on a watch glass in the fume hood, until all acetone had evaporated.

For one series of samples, the washing was followed by dialysis to remove salts from the cellulose ether thickener. This was done by creating a solution of 1 wt% (0.05 mM) polymer in water as described above. The polymer solution was added to a standard RC tubing dialysis tube (Spectra/Por®, Repligen Corporation, Waltham, MA, USA) which was 40 mm wide and had a diameter of 255 mm. This was cut into tubes of approximately 1 m. About 500 ml of the polymer solution was poured into each tube which was closed with clips at each end. These membranes were put into a bucket along with deionized water that covered the tubes. The water was changed twice a day for the first four days and then once a day until the 14th day. The conductivity was measured before changing of the water and decreased over time. Subsequently the dialyzed dispersion was freeze dried using an Alpha 1-2 (Martin Christ Gefriertrocknungsanlagen GmbH, Osterode am Harz, Germany).

3.2.3 Rotational rheometry

Rheological measurements were performed to investigate the surfactant concentrations of the dispersions to determine which were relevant to further study using other methods. It was also decided whether the polymer should be dialyzed, washed, or unwashed using this method.

The solutions were made with 2 wt% (0.1 mM) polymer and varying surfactant concentrations, and were left to stabilize for at least three days for accurate rheological results. The polymer-surfactant solutions were weighed to 20 g.

The rheological experiments were performed on a Discovery HR-20 rotational rheometer (TA Instruments, New Castle, DE, USA) and a stainless steel cone-and-plate geometry with a diameter of 40 mm and a cone angle of 4° (CP40-4) was used. Peak hold measurements were performed for all samples and each measurement, the samples went through a conditioning step in which the temperature was set to 20 °C and soaked for 30 s, and it was presheared for 20 s in 10 Pa. The sample was then equilibrated for 60 s before the measurement. The measurements were performed at 20 °C for 120 s at a shear rate of 1.6 s^{-1} and 12 points were measured. The solutions were added to the plate using a cut-off pipette, to minimize shear forces during application.

3.2.4 Du Noüy ring tensiometry

Surface tension measurements were performed to investigate the CAC of the systems including polymer (HM-MEHEC) and surfactant.

The polymer-surfactant solutions had a concentration of 0.5 wt% (0.025 mM) polymer and varying concentrations of surfactants, depending on the CMC of the studied surfactant.

A Sigma 70 tensiometer (KSV Instruments Inc., Monroe, CT, USA) was used with a 765 Dosimat (Metrohm, Herisau, Switzerland) to add polymer-surfactant solution to the measured volume. A standard platinum-iridium ring with a diameter of 9.545 mm, a wire diameter of 0.185 mm, and a wetted length of 119.946 mm was used. The heavy phase was set to water and the gas phase air, with the respective densities added by the system (0.9986 and 0.0013 g/cm^3, respectively). Each measurement also started with measuring the surface tension of the polymer solution before adding the polymer-surfactant solution. The starting volume was 10 ml. The continuous measurements were executed by the addition of the polymer-surfactant solution, volume wise, via the Dosimat to produce a curve with 5 points per decade. After each addition, the solution was stirred for 60 s followed by stabilization for 120 s prior to measuring

the surface tension. The maximum deviation was set to 0.10 mN/m.

3.2.5 Static multiple light scattering (SMLS)

To determine the stability of dispersions containing polymer, surfactant and latex, visual inspection and BS were performed. Photographs were taken on the day the dispersions were created and for two consecutive days. BS measurements were performed on those days as well, using a Turbiscan (Microtrac Formulaction, Toulouse, France), using a wavelength of 850 nm at room temperature. BS profiles were recorded.

The dispersion used with this method were 20 g of the prepared latex dispersions with a polymer concentration of 0.5 wt% (0.025 mM) and a dry latex concentration of 20 wt%, as described above. The surfactant concentrations varied.

3.2.6 Dynamic light scattering (DLS)

DLS measurements were carried out using a Zetasizer Pro (Malvern Panalytical Ltd., Malvern, UK). These samples were prepared by diluting latex-polymer-surfactant dispersions, so that the dry latex concentration was 0.2 wt%, and the polymer and surfactant concentrations constant. Therefore, these samples were created in a similar way as previous samples by mixing the latex dispersion with stock solutions of 0.5 wt% (0.025 mM) polymer and 1 wt% surfactant. From these 20 g samples, the dispersions were transferred each day to cuvettes using a pipette and were taken from the middle of the containers to avoid the precipitate at the bottom.

Measurements were performed at 20 ° C, with a 30 s equilibration time, and each sample was scanned five consecutive times. The angle of detection was set to back scatter and the wavelength was 633 nm. The average of the five scans was plotted for the analysis.

The choice of the dispersant parameters, n and η, significantly affects the results and were chosen depending on the sample. The chosen parameters are presented in Table 3.3.

Table 3.3: Choice of parameters for the dispersant during the DLS measurements, depending on the dispersed components.

Dispersed components	n	η (mPa·s)
Latex	1.33	1
Polymer	1.33	25
Surfactant	1.33	1
Latex & polymer	1.33	25
Polymer & surfactant	1.33	25
Latex, polymer & surfactant	1.33	25

4 Results and discussion

The components included varied between the different methods. In all methods, both polymer and surfactant were included since the interaction between these was the main aspect of the study. The association between them and the rheological behavior was expected to depend on the structures of the polymer and surfactant as well as the surfactant concentration. Therefore, rheological and CAC measurements were performed.

BS and DLS measurements also included the latex to be able to measure the stability using light scattering. This was also important for the investigation of polymers and surfactants in systems more similar to the paint application. Aggregation of the polymer-surfactant clusters to the latex particles was expected and consequently, a phase separation. The effect of the surfactant concentration was investigated.

The polymer interaction was expected to depend on DS_{methyl}, and this should be seen in the rheological and BS results, since these were the methods with which the comparison was performed.

The surfactants were expected to have varying properties depending on the present groups in the structure. The presence of an amide group was expected to lower the CMC and increase the surface tension at the CMC. The solubility was expected to increase with the number of EO groups and with a shorter alkyl chain. Branching was predicted to have less efficient packing at the interface and thus, weaker interaction with the polymer. Increased chain length was expected to lower the CMC. No predictions were made for the presence of PO.

4.1 Rheological behavior of polymer-surfactant solutions

4.1.1 Effect of salt and unreacted hydrophobe

The polymers were expected to be affected by unreacted hydrophobe, DS_{methyl}, and the presence of salt in the system. By measuring the rheology of systems containing 2 wt% (0.1 mM) HM-MEHEC, various pretreatments of the polymer were compared, and the effect of unreacted hydrophobe and presence of salt on the polymer was evaluated. The nonionic surfactants were expected to not be affected by the presence of salt and their structures were only investigated for acetone washed polymer samples.

Figure 4.1 displays the effect of the polymer pretreatment, comparing systems containing HM-MEHEC and LC(10-16)AO10. The untreated polymer gives a high viscosity at low surfactant concentrations while the acetone washed polymer results in a lower viscosity

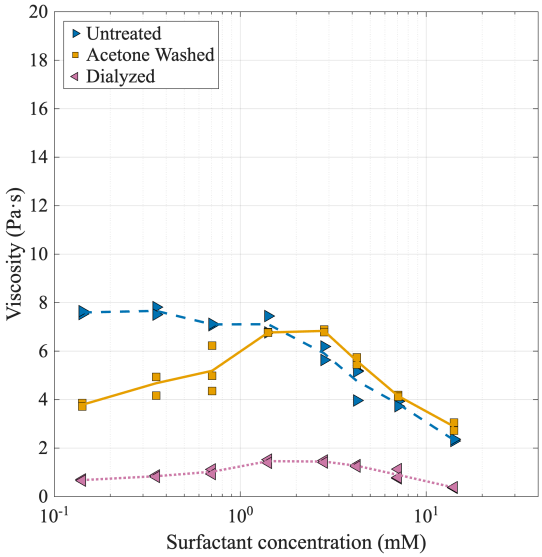


Figure 4.1: Viscosity for the systems containing 2 wt% HM-MEHEC, with different pretreatment, and LC(10-16)AO10. The lines are guides for the eye and the multiple values for each concentration were taken to achieve the most accurate viscosity value for each concentration.

in this range. The shape and peak of the dialyzed curve is similar to that containing the acetone washed polymer but the viscosity is lower for all points.

The data suggest that the unreacted hydrophobe and other acetone soluble materials affect the system at lower surfactant concentrations, and that the presence of salt has a less significant effect on the network formation with surfactant. Yet it has an overall important effect. One possible explanation is that the unreacted hydrophobe causes the increased viscosity because it has a structure similar to a very hydrophobic surfactant, with a very low CAC. This means that the peak of the curve should appear at lower concentrations than investigated. The behavior would extend the polymer network and shift the onset of LC(10-16)AO10 adsorption, or the CAC, to lower concentrations. However, after the CAC of the acetone washed system (approximately 2 mM), the systems behave similarly and the network is not affected by the unreacted hydrophobe. The longer polymer chains dominate the interaction at higher surfactant concentrations.

The similar shape of the curve for the dialyzed system may indicate that the polymer-surfactant complex is not notably affected by the presence of salt. The lower viscosity is observed over the range of surfactant concentrations and could be a consequence of decomposition of the polymer. The preparation of polymer with this treatment was significantly more time consuming, which allowed for the decomposition to happen. The polymer was dialyzed for two weeks, freeze dried, and dispersed for about four days, instead of a few hours for the other polymer treatments. The decomposition suggests smaller polymer molecules that would indicate a network with

more connection points, where the physical bonds can be broken. This is probably what caused the lower viscosity and not the removal of salts. This remains to be confirmed by for example GPC.

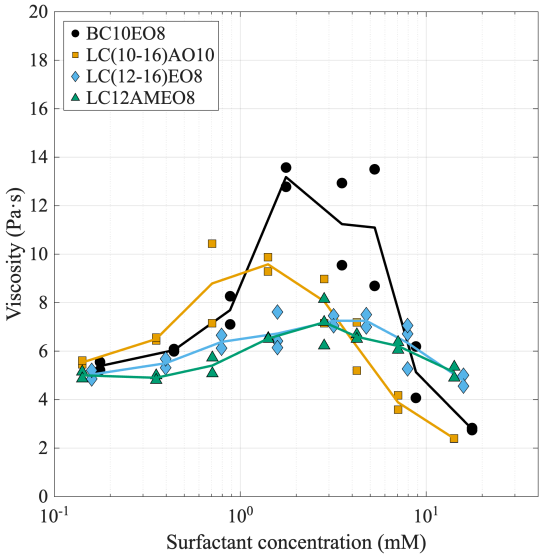
In summary, the treatment of the polymer affects the viscosity of the system, and the removal of the side products from the polymer seems to have a more significant impact on the interaction with the surfactant than removing the salts. Therefore, the polymer was acetone washed for the rest of the measurements and methods.

4.1.2 Effect of polymer methyl substitution

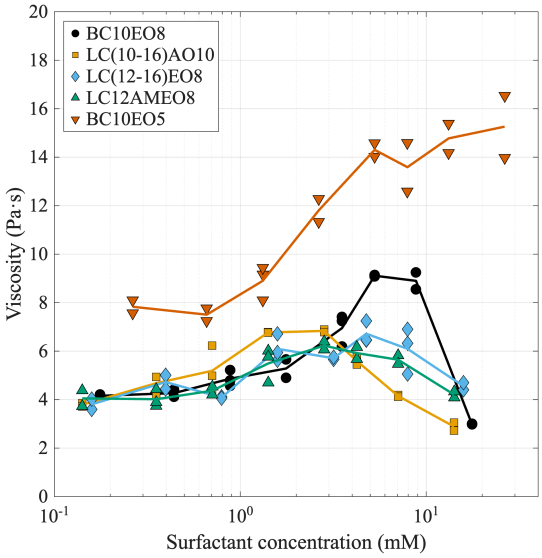
The effect of DS_{methyl} on the system was investigated by measuring the rheology of varying surfactant concentrations for all five surfactants and the two polymers.

For systems containing HM-EHEC, all surfactants behave differently, as can be seen in Figure 4.2a and Table 4.1. LC surfactants have lower viscosity than BC10EO8 at surfactant concentrations between 1 and 10 mM. LC(10-16)AO10 has a viscosity that is significantly higher for BC10EO8 for concentrations up to 1 mM. However, the viscosity for BC10EO8 decreases shortly after the peak and ends close to the viscosity of LC(10-16)AO10, and is lower than for the two other surfactants with 8 EO.

When using the HM-MEHEC, the viscosity is similar for all surfactants except



(a) Systems containing HM-EHEC and four surfactants.



(b) Systems containing HM-MEHEC and five surfactants.

Figure 4.2: Viscosity variations depending on the surfactant, the surfactant concentration and the type of polymer. The number of points at each concentration is at least two, but for results with a deviation between the points of more than 0.5 Pa·s, a third measurement was performed to get a more accurate result. The lines are guides for the eye.

Table 4.1: Suggested CAC for the polymer-surfactant systems from the rheological measurements with a polymer concentration of 2 wt%.

Surfactant	$CAC_{HM\text{-}EHEC}$ (mM)	$CAC_{HM\text{-}MEHEC}$ (mM)
BC10EO8	1.8	8.8
BC10EO5	-	-
LC(10-16)AO10	1.4	1.4
LC(12-16)EO8	4.0	4.8
LC12AMEO8	2.8	2.8

BC10EO5, but the position of the peaks differ, as shown in Figure 4.2b. Both BC surfactants show higher viscosity than the LC surfactants at concentrations above 5 mM. However, BC10EO8 behaves similarly to the LC surfactants until the peak at approximately 9 mM.

Comparing the polymers, most surfactants behave the same with both polymers but the viscosity is slightly higher for the systems containing HM-EHEC. LC(12-16)EO8 and LC12AMEO8 have a similar viscosity and concentration dependence for both polymer systems, indicating that the presence of methyl on the HM-MEHEC does not affect their interaction with the polymer. In fact, the CAC for LC12AMEO8 is the same for both systems and for LC(12-16)EO8 they are very similar.

BC10EO8 however, has a significantly decreased viscosity when interacting with HM-MEHEC and the CAC is very different (1.8 and 8.8 mM). This indicates a stronger adsorption to the other substituted groups on the AHG than the methyl groups and that the presence of the methyl groups weakens the interaction, and consequently polymer network. The wide peak suggests a stronger network, compared to the other systems, but the quick viscosity decrease indicates a fast separation above the CAC.

LC(10-16)AO10 also behaves differently for the two systems. The viscosity is higher when using HM-EHEC but the CAC is the same (1.4 mM). The methyl substitution affects this surfactant in a similar way as BC10EO8 and it has a weaker interaction when methyl groups are present, but the interaction happens at a similar surfactant concentration for both polymer systems. The system also appears to have a larger concentration range for stronger interactions and a fast drop in viscosity above the CAC.

To summarize, an increased DS_{methyl} results in a decreased viscosity and a decreased CAC for the surfactant with a branched chain and the surfactant with PO in the head group. The polymer network can be stronger at certain concentrations for polymers with lower DS_{methyl} but it decreases quickly. The choice of surfactant concentration is more important for combinations of HM-EHEC and surfactants with branched chains and PO groups, to achieve the desired viscosity compared to systems containing HM-MEHEC.

4.1.3 Effect of surfactant structure

The effect of the surfactant structure on the interaction was investigated by measuring varying surfactant concentrations with the two polymers using rotational rheometry. The presence of amide was expected to decrease the CMC, indicating a lower CAC as well. The solubility of the surfactant was predicted to increase with an increasing number of EO groups and a smaller alkyl group, suggesting improved interaction with the polymer. BC surfactants were expected to be less efficient at interfacial packing, implying an increased viscosity.

The surfactants behave differently depending on their structure and concentration dependence when interacting with the polymers. LC(12-16)EO8 and LC12AMEO8 show a small variation in viscosity at different surfactant concentration which indicates weaker association with the polymers than the other surfactants, and that the network is relatively easy to break. The CMC, and consequently the CAC, for LC12AMEO8 was lower than all other surfactants except LC(10-16)AO10 when using HM-EHEC.

LC(10-16)AO10 gives a higher viscosity of the polymer systems than the other LC surfactants, but lower than the BC surfactants. The CAC is lower than for all other polymer-surfactant systems, for both polymers, as well as a wider peak in viscosity. Increased DS_{methyl} makes it behave more like the LC surfactants without PO, but it still keeps the lower CAC.

BC10EO8 gives a higher viscosity than the LC surfactants, but lower than BC10EO5. Although, there is a wide spread of viscosity values at concentrations after the CAC, especially for the HM-EHEC system. The CAC is intermediate for the HM-EHEC system and the highest (for the systems that have a CAC) for the HM-MEHEC system. An important note is that the BC10EO8 samples were measured 7 days after the preparation of the samples, instead of 3 days after, as the other surfactants. This time can have an effect on the system since it is possible that polymer breaks down over time, as the dialyzed polymers most likely did. However, the behavior is similar to that of the other surfactants at low concentrations and to the other BC alcohol ethoxylate (BC10EO5) at intermediate concentrations. This indicates that the system probably stabilized and that the polymer had not degraded significantly.

BC10EO5 does not have a peak in viscosity within the range that the other surfactants have, and seems to continuously increase. In Figure A.1, the viscosity at higher concentrations are presented. It was decided not to perform any further measurements with this surfactant because of this behavior. A phase separation, that can be observed in Figure 4.3, also occurred in all samples using this surfactant. This probably depends

on the low water solubility of the surfactant because of the low polarity.

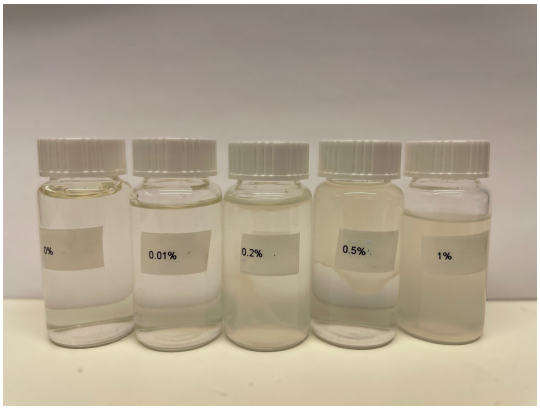


Figure 4.3: Phase separation in samples for rheometer with 2 wt% HM-MEHEC and varying concentration of BC10EO5.

A note on the measurements using HM-EHEC for BC10EO8 and LC(10-16)AO10 is that these measurements accidentally were performed with settings for plate and plate, instead of cone and plate. A reference measurement was performed, using the 0 wt% sample and cone and plate, and the previously measured viscosity was corrected to obtain viscosity in the correct range. The correction increased the viscosity.

The presence of an amide group in LC12AMEO8 was expected to modify the self-assembly, and consequently the CAC of the system, and it did compared to the corresponding surfactant without amide, LC(10-12)EO8. The only polymer-surfactant system with a lower CAC when using HM-MEHEC is LC(10-16)AO10, but both that and BC10EO8 has lower values for the HM-EHEC system.

The solubility and interaction was predicted to increase with the number of EO groups and it it did. BC10EO5 phase separated immediately and the viscosity only increases with surfactant concentration. BC10EO8 shows a totally different behavior and the data suggests that the difference in EO units, of only three, between these surfactants is enough to make BC10EO5 hydrophobic enough to not dissolve. The implication is that the polymer network never separates with the increased surfactant concentration for BC10EO5 since there is not enough surfactant dissolved to interact with the polymer.

The hypothesis of an increased solubility with a smaller alkyl group is difficult to determine because of the small variations in alkyl groups and the chain length distributions of the surfactants. No significant effects are observed.

The BC surfactants were expected to have a higher viscosity because of less efficient packing at the interface, and this is true for a concentration range. In the HM-EHEC system, the viscosity was generally higher between 1 and 10 mM, and in the

HM-MEHEC system it was higher between 2 and 10 mM. This indicates a stronger adsorption of BC surfactants at the polymer surface at these concentrations. At the other concentrations, it had similar effects to LC surfactants. However, there are some signs that an increased surfactant concentration leads to a faster separation of the polymer network with the BC surfactants compared to the LC surfactants.

The presence of PO was expected to have an effect and the results using LC(10-16)AO10 indicates a peak in viscosity at lower surfactant concentrations. This suggests that the PO is a less hydrophobic moiety in the system which makes it reach CAC earlier than for the surfactants without this group.

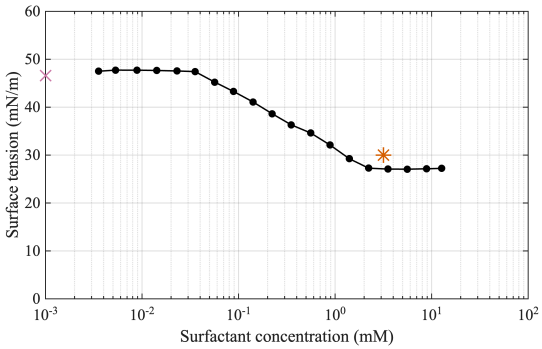
To summarize, the structure of the surfactant affects the viscosity of the studied system. The presence of an amide group does not give the lowest CAC of all surfactants, as expected, however it was not the lowest. An increased number of EO groups increased the solubility and weakened the adsorption, but the same hypothesis for shorter alkyl groups could not be confirmed. The BC surfactants showed higher viscosity and stronger adsorption for a certain concentration range but not for all surfactant concentrations. The presence of PO in the polar head resulted in a lower CAC, suggesting a more dynamic system.

4.2 Surface tension behavior and polymer-surfactant association

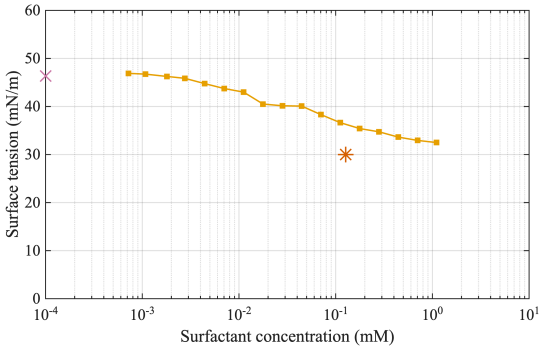
Surface tension measurements were performed using Du Noüy ring to determine CAC of the polymer-surfactant systems. Only HM-MEHEC was used with four of the surfactants. The effect of the surfactant structures is investigated related to the presence of an amide or PO group and the hydrophobic chain branching.

The measurements were difficult to perform because of the low surfactant concentrations required. Especially for surfactants with a CMC lower than 1 mM (see Table 3.2) since the CAC should be lower than the CMC. This proved difficult because of the small additions of polymer-surfactant dispersion, where the volume was so small that it did not fall into the solution but remained at the tip of the needle. This means that the concentration of surfactant might be lower than calculated and that the addition of the dispersion might be too high at later concentrations, causing a larger decrease in surface tension at the higher concentration.

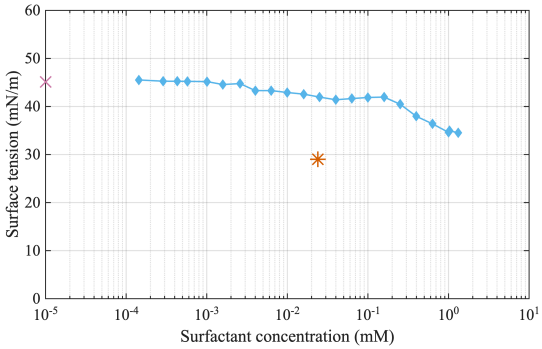
Measurements using BC10EO8 resulted in Figure 4.4a which appears to be a CMC curve and the HM-MEHEC is not affecting it noticeably. The surface tension passes that of the pure surfactant close to the CMC, and the final surface tension is very close to the literature value. The HM-MEHEC does not seem to have a significant effect on the



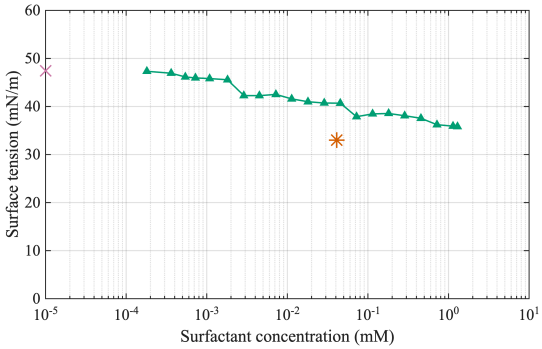
(a) System containing BC10EO8.



(b) System containing LC(10-16)AO10.



(c) System containing LC(12-16)EO8.



(d) System containing LC12AMEO8.

Figure 4.4: Results from the surface tension measurements for systems containing 0.5 wt% HM-MEHEC and various surfactants. The ”X” on the y-axis represents the surface tension of the dispersion containing only 0.5 wt% HM-MEHEC, and the ”*” represents the CMC and the surface tension of the pure surfactant.

surfactant in solution at these proportions (0.5 wt% polymer and the presented surfactant concentrations) and no CAC can be found.

LC(10-16)AO10 proved difficult to use for these measurements because of the low concentrations but a CAC might be detectable. At approximately $2 \cdot 10^{-2}$ mM (Figure 4.4b), there is a drop in surface tension and a small plateau. The suggested CAC for the studied polymer systems are presented in Table 4.2. The surface tension is decreasing from the surface tension of the polymer solution, and a CAC at this concentration would be reasonable since it is close to the CMC. The surface tension of the pure surfactant is never reached and there is no second plateau that could represent the CMC. This could be understood as a continuous adsorption of surfactant in the polymer.

Results for measurements with LC(12-16)EO8 are presented in Figure 4.4c. It is possible that there is a CAC around $4 \cdot 10^{-3}$. The last point in the graph was measured by performing a second measurement using 10 ml of the dispersion from the first ($c \approx$ 1 mM) and adding it to a new vessel. Because of the low concentration of the added solution, and a lack of time, only this point and the beginning of another could be measured. The last point did not give a reliable result because the measurement was

Table 4.2: Suggestion of the approximate CAC for the polymer-surfactant systems from the surface tension measurements. The polymer is HM-MEHEC and concentration is 0.5 wt%.

Surfactant	CAC (mM)
BC10EO8	-
LC(10-16)AO10	$2 \cdot 10^{-2}$
LC(12-16)EO8	$4 \cdot 10^{-3}$
LC12AMEO8	$3 \cdot 10^{-3}$

very unstable. However, it seemed to have a similar surface tension to the concentration of 1 mM. This means that the CMC probably has increased from 0.02 to 1 mM for the polymer-surfactant system.

In Figure 4.4d at least one plateau before the CMC can be observed for LC12AMEO8, which could mean that the CAC is about $3 \cdot 10^{-3}$ mM. It is also interesting that the surface tension is higher than for the pure surfactant at, and above the CMC, for this surfactant too. The plateau at approximately 10^{-1} is close to the CMC but the higher surface tension is of note.

The hypothesis of the amide group lowering the CMC and increasing the surface tension at the CMC when interacting with the polymer, is partly confirmed through the behavior of LC12AMEO8 in 4.4d. The surface tension at the CMC is higher than for the pure surfactant and the CMC is very similar. Since the only surfactant to reach the CMC (BC10EO8) has a higher CMC, these results suggest that the CMC changes for the polymer-surfactant system changes from the pure surfactant. The CMC is lower for LC12AMEO8, since it is reached. Additionally, the presence of a potential CAC plateau indicates a predictable behavior of the system. Compared to the other surfactants, the surface tension is similar, but the curve is more similar to the predicted CAC behavior.

A BC was expected to increase the surface tension and the opposite is presented. BC10EO8 is the only studied surfactant to achieve a surface tension below that of the pure surfactant and that show no CAC plateau. The data suggest a very dynamic system where the surfactants never associate with the polymer and only self-associate into micelles. This could indicate that the BC prevents the adsorption to the polymer and that the adsorption of surfactants to the polymer would not be advantageous for the surface tension.

The presence of a PO group, in LC(10-16)AO10, shows a shorter CAC plateau than the other surfactants but it is more prominent (4.4b). The CMC is never reached but it is not for the similar LC(12-16)EO8 (4.4c), without PO, either. One possible explanation could be the chain length distribution of these surfactants that could result in a less predictable adsorption to the polymer. The surfactants with longer chain lengths could be more prone

to adsorb to the polymer, resulting in a higher surface tension when they are unimers in solution.

That three of the surfactants did not reach the surface tension of the pure surfactant suggests that the dynamics for the systems are altered. The increased surface tension suggests that the surfactants have not reached the surface and are interacting with the polymer. This could be explained by the increased viscosity because of the presence of the polymer.

Summarizing these results, the presence of an amide group shows a lower CMC than the other surfactants, and results in the most predictable behavior of the studied systems. The BC surfactant suggests a dynamic system where there is no strong adsorption to the polymer at the studied concentrations. The presence of PO did not result in major results but suggests an impact from chain length distribution on the system dynamics. The high surface tension indicates slower dynamics of the systems than predicted.

4.3 Colloidal stability of latex-polymer-surfactant dispersions

When adding latex to the dispersions of surfactant and polymer, the stability of the systems is observed with BS. The hypothesis was that there would be a desired bridge flocculation at low surfactant concentration and an undesired depletion flocculation at an increased concentration. It was expected that there would be a difference between the two polymers and the four surfactants studied. No specific predictions were made for the structure of either component.

The comparison is done using wt% of the components.

From Figure 4.5 it is clear that all three-component systems, with varying surfactants and surfactant concentrations, separated during the first 24 hours. Figure 4.6 shows the BS results that indicate the same behavior for systems containing 0.5 wt% HM-EHEC and LC(10-16)EO8. All surfactants displayed the same behavior.

(a) Day of preparation. **(b)** Day after preparation. **(c)** Two days after preparation.

Figure 4.5: Samples for BS, containing 20 wt% dry latex, 0.5 wt% HM-EHEC and 0, 0.01, 0.05, 0.1, and 0.5 wt% LC(10-16)AO10 from the day of preparation to two days later.

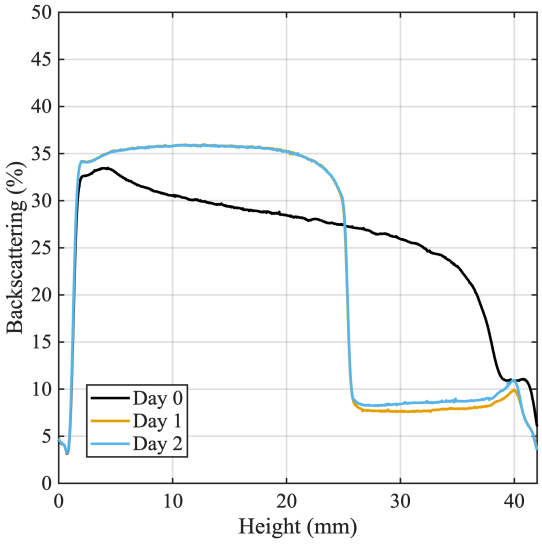
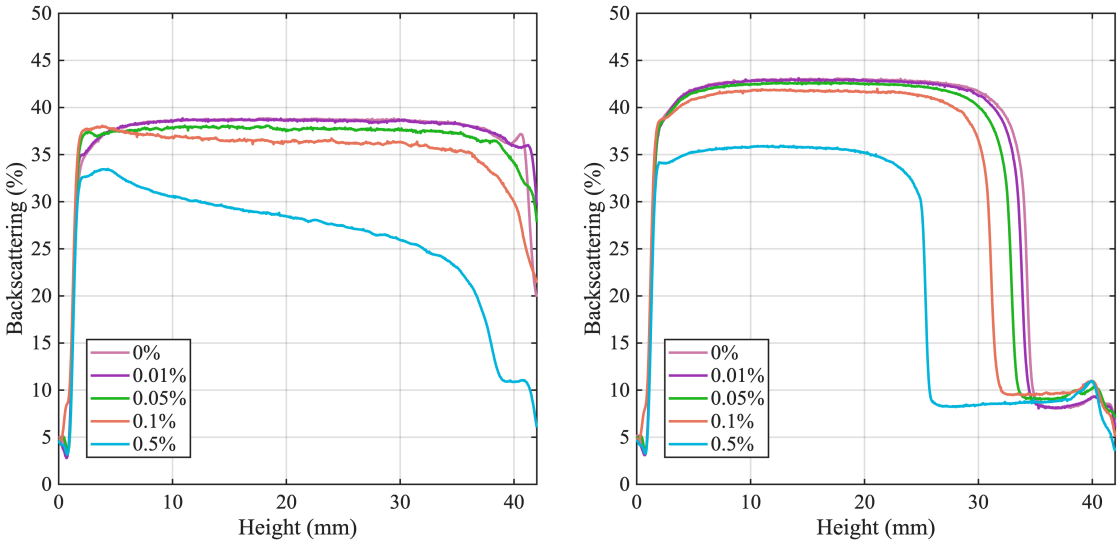


Figure 4.6: BS of a latex-polymer-surfactant dispersion over two days. The dispersion contained 20 wt% dry latex, 0.5 wt% HM-EHEC and 0.5 wt% LC(10-16)EO8. Day 0 is the day of preparation.

Figure 4.5 and 4.7 both show that an increase in surfactant concentration is connected to a smaller bottom phase (approximately 34 mm for 0.01 wt% and 25 mm for 0.5 wt%) and decreased BS after the separation. These figures are also similar for all the studied systems.



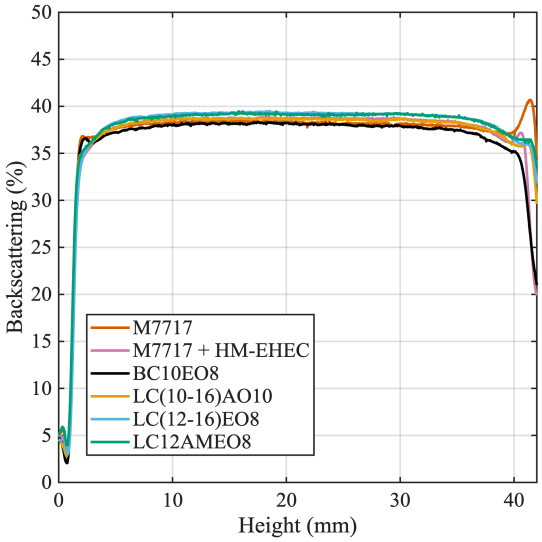
(a) The day of preparation.

(b) Two days after preparation.

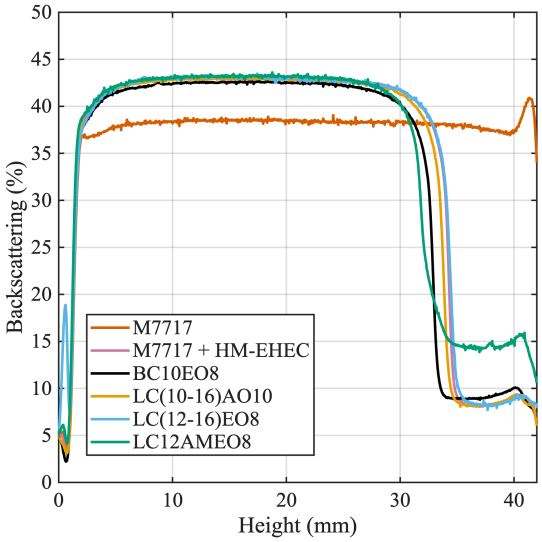
Figure 4.7: BS of the samples containing 20 wt% latex, 0.5 wt% HM-EHEC and various concentrations of LC(10-16)AO10 the day of preparation and two days later.

Figure 4.8 compares the surfactants the day of preparation for 0.01 wt% (4.8a and 4.8b) and 0.5 wt% surfactant (4.8c and 4.8d). References with only latex (M7717) and a latex-polymer system (M7717 + HM-EHEC) are included. No significant changes are observed between the surfactants after separation and has occured, and the latex is stable

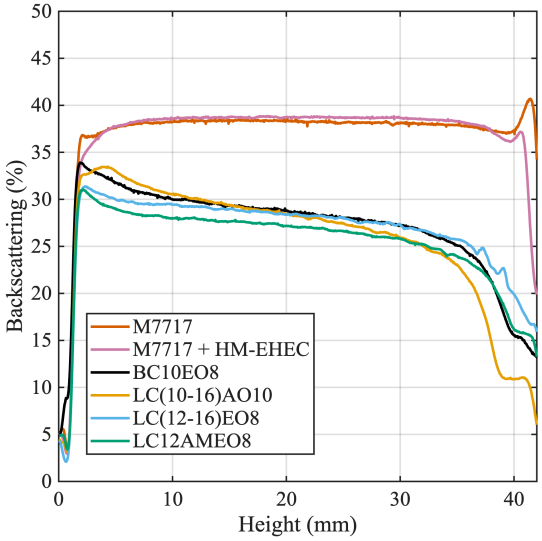
over time. The latex-polymer system is more stable than any latex-polymer-surfactant system, and the dispersed latex is more stable than the latex-polymer systems. The small differences between the surfactants are that LC12AMEO8 has a slightly higher BS above 35 mm than the other surfactants using HM-EHEC (Figure 4.8b) and LC(12-16)EO8 has a slightly lower BS within the same height range when using HM-MEHEC (Figure B.1b). This is probably due to the time between the measured samples and no clear conclusions can be drawn.



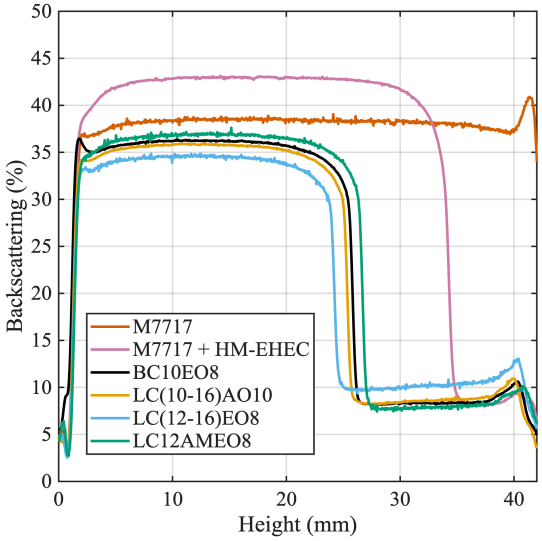
(a) 0.01 wt% of various surfactants on the day of preparation.



(b) 0.01 wt% of various surfactants two days after preparation.



(c) 0.5 wt% of various surfactants on the day of preparation.



(d) 0.5 wt% of various surfactants two days after preparation.

Figure 4.8: Graphs showing BS over time of dispersions containing 20 wt% dry latex (M7717), 0.5 wt% HM-EHEC, and various surfactants at concentrations of 0.01 and 0.5 wt%, taken on the day of preparation and two days later. Latex-only and latex–polymer dispersions are shown as references.

The separation clearly occurs during the first 24 hours after preparation, and for the highest surfactant concentration (0.5 wt%) it starts immediately after preparation. The flocculation observed is likely the undesired depletion flocculation and since all solutions contain the same amount of latex, which in itself is stable over time, presence of surfactant worsens the stabilization of the system. This should be because of a stronger association of polymer-surfactant complexes to the latex at surfactant concentrations below 0.5 wt% and that it decreases between 0 and 0.5 wt%. There might be some bridging flocculation at the concentrations below 0.5 wt% since they do not separate immediately. Another reason could be that the surfactant that stabilizes the latex is displaced by the added surfactant, this would also decrease stability.

In summary, the latex separation increases with surfactant concentration and the separation occurs during the first 24 hours after preparation. The increased separation with increased surfactant was expected and no significant differences were seen between the surfactants for the studied compositions. Depletion flocculation is likely the explanation for the separation.

4.4 Aggregation behavior in latex-polymer-surfactant dispersions

The DLS measurements were performed to study the aggregation behavior of systems containing latex, HM-MEHEC, and either BC10EO8 or LC(10-16)AO10. Differences in size between the components and systems were observed by comparing single, and two components systems and systems with varying surfactant concentration. The stabilization was also observed by comparing sizes for two days and it was expected that there would be differences between the days due to aggregation of latex. A difference between surfactants and surfactant concentration was expected.

The complex systems made results difficult to analyze, and it was concluded that no further testing would be performed. Specifically, the solutions with all three components are difficult to analyze because of the wide spread of molecular shapes and sizes. Therefore, only the graphs and approximate sizes of the clusters are analyzed. The hydrodynamic diameter and polydispersity index are not reliable parameters, except for the latex, since the method assumes spherical structures, and the polymer and the formed aggregates are not spherical. The specific intensities are not compared because of the method's favoring of the larger particle sizes. Instead, the relative changes in peak position are analyzed.

In Figure 4.9, the sizes of the components in samples containing one or two components, dispersed in water, are presented. The single-component samples, with latex or surfactants dispersed in water (Figure 4.9a and 4.9b), give clear peaks at certain sizes

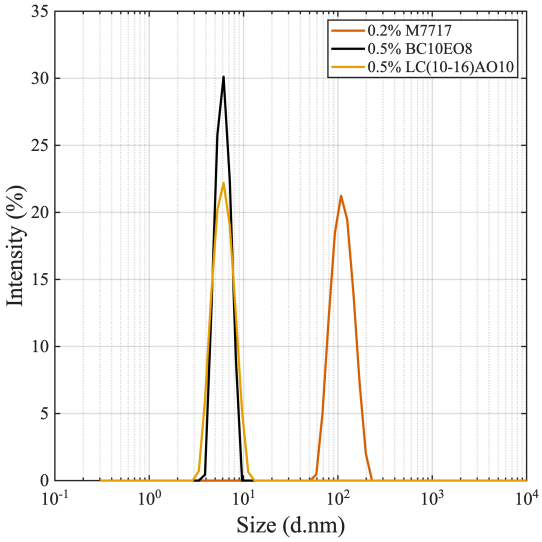
indicating the particle size of the latex and micelles, respectively. This is approximately 100 nm for the latex and 6 nm for both surfactants. Comparing Figure 4.9a and 4.9b, these sizes do not change over time. The polymer-surfactant samples are stable over time, but the latex-polymer sample indicates that the polymer either adsorbs to the latex over time or separates, forming an aggregate (Figure 4.9c and 4.9d). This reasoning can be done by comparing the curve of the polymer in itself to that combined with the latex, where the peak of the latex particle dominates.

When studying systems with increasing surfactant concentrations of BC10EO8 in Figure 4.10, notable changes are observed between the samples from the day of mixing to two days later. It appears that the samples stabilize over the days, but it is also important to note that there was separation in the samples already a day after preparation, as can be seen from the BS results. This could indicate that these results do not include larger particles since they sediment at the bottom, and only the top phase was analyzed.

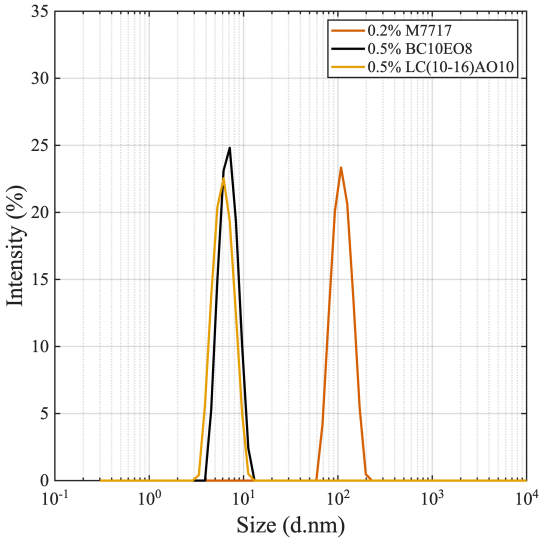
The results for LC(10-16)AO10 show a similar behavior to BC10EO8 over the days, where the samples seems to stabilize. These results are presented in Figure 4.12. However, the surfactant concentration displaying the largest particle sizes changes from 0.5 wt% surfactant to 0.1 wt%, at least for the day of preparation. The sizes increase for concentrations above 0.01 wt% and then decrease for 0.5 wt%. As can be seen in Figure 4.11, there was a clear separation in the 0.05 and 0.1 wt% samples the day after preparation and therefore these were the only samples containing surfactant investigated this day.

The results from the one and two component systems indicate the stable latex and micelle sizes over the days. It is also clear that the polymer significantly affects the sizes of the clusters in solution by comparing the distribution for samples containing only polymer and those containing polymer and either latex or surfactant. For samples containing both polymer and surfactant, the results are more similar to those of the polymer in solution than the surfactant in solution. When latex and polymer are combined, the location of the intensity peaks is more similar to that of the latex, which is expected since the polymer should adsorb to the latex particle. The intensity peak at the latex location is also broader with polymer present, which also indicates polymer adsorption to the latex. Over time, the polymer-surfactant systems are stable but the latex-polymer system show slightly increased particle sizes, as expected.

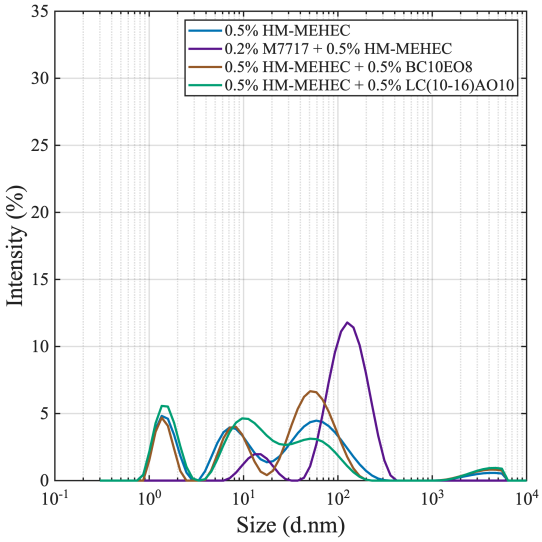
With increased surfactant concentration, an increased particle size is observed for BC10EO8 while the size first increase with an increased amount of LC(10-16)AO10, to 0.1 wt%, and then decrease with a further increase. Also, the higher surfactant concentration, the longer time until the system stabilizes for BC10EO8. This indicates a



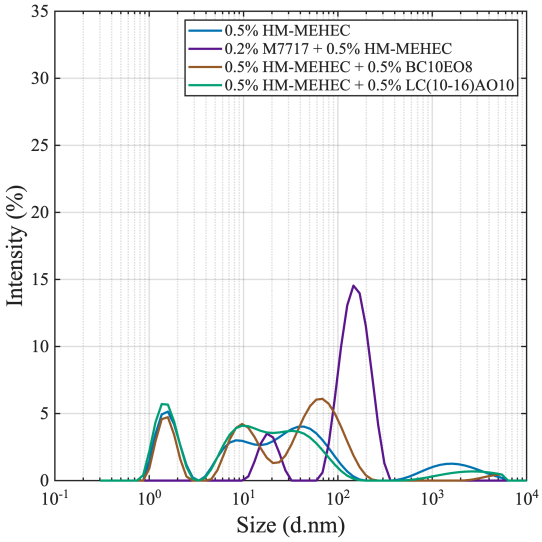
(a) Surfactants and latex dispersed in water the day of preparation.



(b) Surfactants and latex dispersed in water the day after preparation.

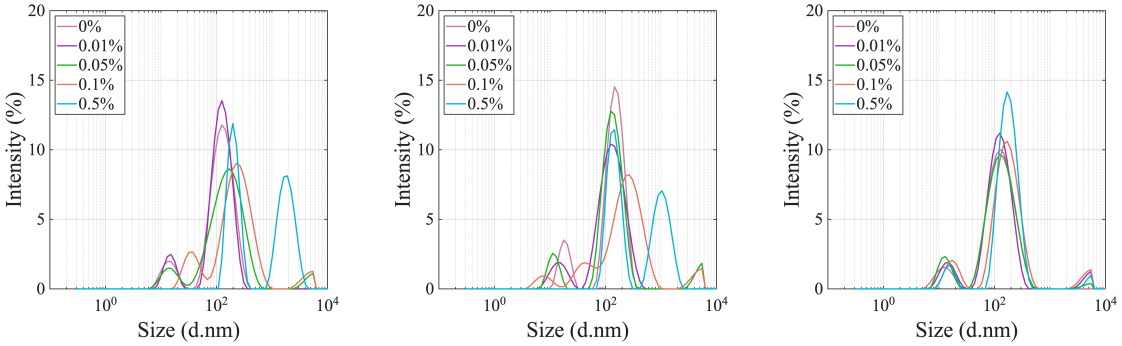


(c) HM-MEHEC and combinations with latex and surfactants, dispersed in water the day of preparation.



(d) HM-MEHEC and combinations with latex and surfactants, dispersed in water the day after preparation.

Figure 4.9: Sizes of the measured components in various combinations the day of preparation and one day later. The components are latex (M7717), HM-MEHEC, BC10EO8 and LC(12-16)AO10, dispersed or dissolved in water.



(a) The day of preparation. **(b)** The day after preparation. **(c)** Two days after preparation.

Figure 4.10: Size distributions from DLS measurements of dispersions containing 0.2 wt% dry latex, 0.5 wt% HM-MEHEC, and various concentrations of BC10EO8 for the day of preparation to two days later.

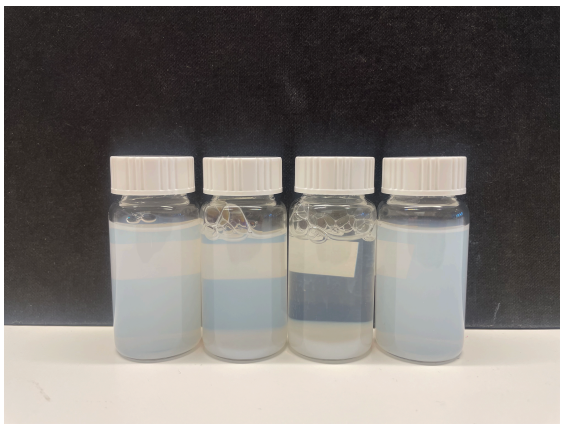


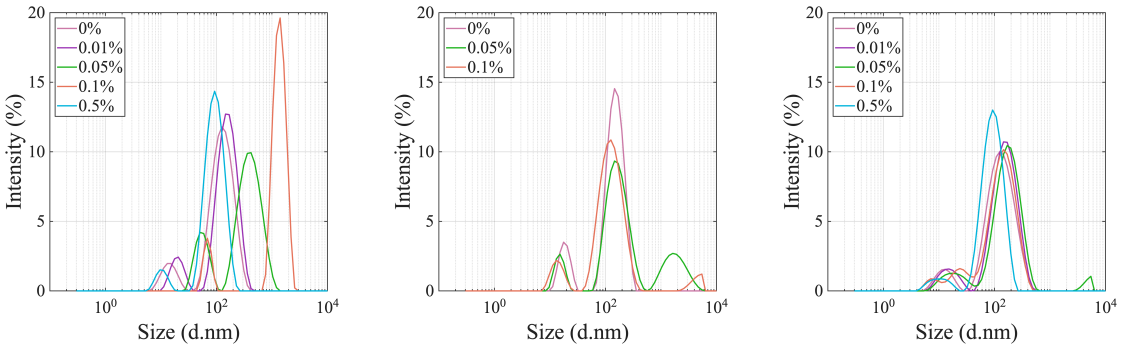
Figure 4.11: DLS samples the day after prepration where the separation is observed.

dynamic system where the polymer adsorbs to the latex particle, which is expected. This might be what contributes to the increased depletion flocculation seen in the BS measurements. Larger particles that are formed faster should aggregate faster, resulting in rapid phase separation observed with increased surfactant concentrations for BC10EO8, and at 0.1 wt% for LC(10-16)AO10. However, the phase separation has to be taken into account. The measurements were performed on the upper phase and larger aggregated particles might not be detected.

The difference between the surfactants can be due to the presence of PO or the branched chain.

The sizes above 2000 nm, seen in all combination of the components, are some larger aggregates.

In short, the systems behave as predicted, the polymer seems to induce phase separation and the polymer and surfactant adsorb to the latex over time. Increased surfactant concentration consequent in longer stabilization times for the BC surfactant. The



(a) The day of preparation. **(b)** The day after preparation. **(c)** Two days after preparation.

Figure 4.12: Size distributions from DLS measurements of dispersions containing 0.2 wt% dry latex, 0.5 wt% HM-MEHEC, and various concentrations of LC(10-16)AO10 for the day of preparation to two days later.

data suggests that depletion flocculation occurs for all systems and that the clusters in solutions are mainly polymer-surfactant structures adsorbed to the latex, as expected. The presence of PO or a branched chain affects the sizes of the clusters in solution and the surfactant concentration where separation occurs is different for the two investigated surfactants.

4.5 Interactions between polymer and surfactant

Comparing the rheological and surface tension results, it is possible to improve the understanding of polymer-surfactant interactions. The polymer treatment and DS_{methyl} was compared during the rheological results and the surfactant structures and concentrations with both methods.

The treatment of polymer suggests that the polymer network is primarily dependent on the presence of unreacted material and hydrophobe, and not the presence of salt. The adsorption of surfactants to the polymer is especially altered at low surfactant concentrations. The presence of these short polymer segment extends the polymer network and thus, increases the viscosity. Increased DS_{methyl} however, has the opposite effect and the polymer network is weakened and the CAC is lowered, indicating an earlier onset of surfactant adsorption for surfactant with branched chains or PO groups. The network is stronger with a polymer containing methyl groups, for these surfactants, but only for certain concentrations, before the viscosity starts to decrease. The choice of surfactant concentrations are therefore more important for HM-EHEC than HM-MEHEC.

Comparing the surfactant structure with the two methods, indicates different behavior between surfactants. The CAC and CMC is slightly lower for surfactants containing

an amide group, and this surfactant displays the most predictable CAC behavior of the studied surfactants.

BC surfactants are suggested to increase the adsorption to the polymer surface, within a certain concentration range, for rheological measurements, and show a decreased dynamic behavior in surface tension measurements. These results are most likely affected by the polymer concentration. For the rheological measurements, the concentration was 2 wt% (0.1 mM) and for the surface tension measurements 0.5 wt% (0.025 mM). BC10EO8 has a CMC of 3.17 mM (Table 3.2) and displays a CAC of 8.8 mM (Table 4.1) for the HM-MEHEC system in the rheological measurements, and none in the surface tension measurements. These results suggest that the dynamics of BC surfactants are highly dependent on the polymer concentration.

The rheological result suggest that the presence of PO in the surfactant head group increases the affinity of the surfactant and lowers the CAC. The surface tension measurements show similar results and suggest that the chain length distribution might affect the dynamics.

Overall, the polymer structure and surfactant concentration has a more significant effect than the structures of the surfactants on the polymer network and the system dynamics.

4.6 Interactions between latex, polymer, and surfactant

Interactions in the latex-polymer-surfactant systems are studied with BS and DLS. The interactions between latex and polymer-surfactant structures appear to have a more significant effect on both the stabilization and the size of the structures.

BS measurements show no different behaviors between polymers or surfactants and the separation happens during the first 24 hours. The higher the surfactant concentration, the faster the separation. The cluster sizes however, seem to stabilize faster with lower concentrations of surfactant and the polymer-surfactant structures adsorb to the latex particle. Depletion flocculation most likely affects the sizes measured and the overall size distribution might not be recorded because of the measurements of the dispersion and not precipitate.

DLS measurements show a different concentration dependence between BC10EO8 and LC(10-16)AO10 where the separation occurs earlier for lower concentrations for systems containing LC(10-16)AO10 than BC10EO8. The sizes also increase for lower concentrations when LC(10-16)AO10 is used. These results suggest that the PO group or the branched chain affects the associative behavior between the latex, polymer and surfactant. From the rheological results, the PO group was assumed to increase

the dynamics of the surfactant and the similar behavior can be observed in the DLS measurements. The decreased dynamic behavior was suggested for the BC surfactant and this is also similar in the DLS measurements. Therefore, the presence of a PO group seems to affect the stability of the systems because of the increased affinity where the surfactants adsorb to the polymer at lower concentrations.

5 Conclusion

This project aimed at understanding the hydrophobic interactions between cellulose ether thickeners and surfactants used for paint formulations. Various methods were used to study the effect of the interactions on the viscosity, stability, aggregation, and surface tension of solutions and dispersions. The results have been used to understand how the structures of the components affect the interactions in the systems. The test protocols developed in the project will be used in future development work at Nouryon.

The hydrophobically modified cellulose ether thickeners HM-EHEC and HM-MEHEC, were primarily investigated to understand the effect of methyl substitution on the compositions. The results imply that the methyl groups weaken the interaction with all surfactants. The association is stronger and occurs at lower surfactant concentrations for the HM-EHEC compared to the HM-MEHEC. No difference between the two polymers is observed in the stabilization of the latex dispersions, where depletion flocculation seems to be equally present for all surfactant concentrations for the studied times.

In contrast to the two polymers, the surfactants were studied with all methods and their structures affect the results differently for each method. The main difference could be observed between the BC and LC surfactants. The BC surfactants increase the viscosity of the polymer solutions more than the LC surfactants, and the association with HM-MEHEC is weaker than for the HM-EHEC. The presence of PO in the head group indicates a stronger association at low surfactant concentration and a weaker at higher concentrations compared to the LC surfactants with no PO present, according to the viscosity studies. The surfactant affinity increases with the presence of PO. An amide group in the chain shows a stronger polymer association in the surface tension measurements but not in the viscosity measurements. Since the LC surfactants have a chain length distribution, it is difficult to draw any clear conclusions. However, the viscosity is slightly lower and the surface tension is higher, which indicates a stronger affinity.

The surfactant concentrations have a significant effect on the stabilization of the systems containing latex. An increase in cluster sizes of the latex dispersions was detected using DLS. Over time, the size stabilized towards the size of the original latex particles, since the larger clusters were observed to precipitate. The PO containing surfactant induced cluster formation at lower concentrations compared to the BC surfactant.

Overall, the systems studied generated expected results, but the varying concentrations of polymer in the different methods make the results difficult to compare since the surfactant adsorption behavior suggests a dependence on the polymer concentration. It

can be concluded that the choice of surfactant and its concentration are important to customize for the application.

6 Future work

The complex chemistry and multiple components in the systems studied contributed to new questions that would be interesting to investigate in future studies.

Surface tension and DLS measurements using HM-EHEC would be useful to further compare the interactions between the polymers with different methyl substitution. Further measurements using the HM-MEHEC would also be useful to perform with other surfactant concentrations.

Flow curves of the surfactants would contribute to an improved understanding of the interaction with the polymer, especially for the paint application.

The stability of the dispersions would be another relevant factor to further study. Especially the phase separation during the first 24 hours, the stability of higher surfactant concentrations could also be studied to determine if the separation behaves similarly.

The correlation between polymer concentration and surfactant interaction, especially in the stabilization measurements, could also be useful to further understand the interactions.

The new methods and test protocols developed in the project will be useful for future studies of model paint systems.

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A Rheological Measurements

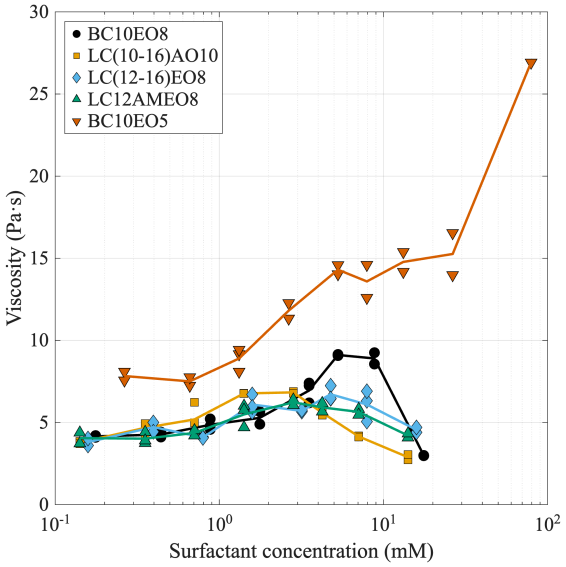
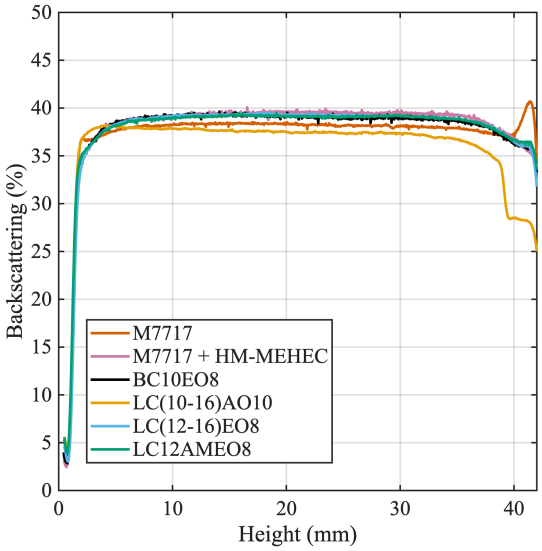
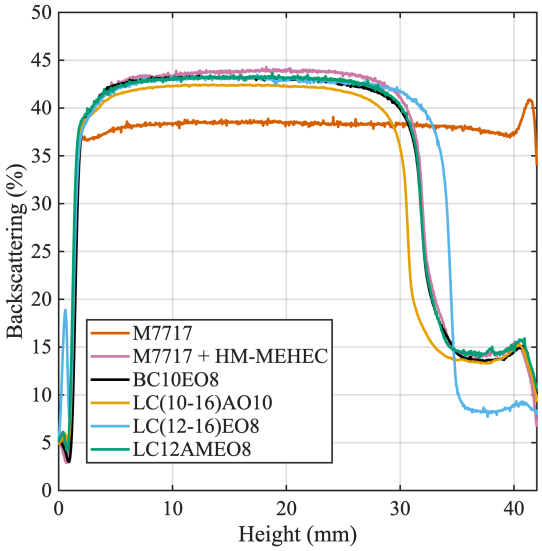


Figure A.1: Measurements of HM-MEHEC and various surfactants, including higher concentrations of BC10EO5 to investigate the continuous increase in viscosity.

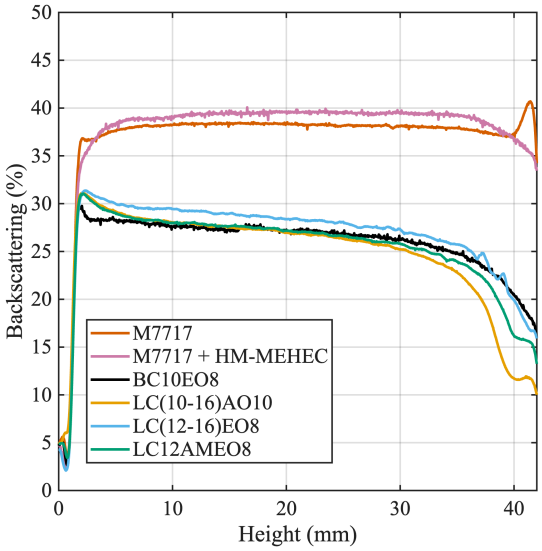
B Stability Measurements



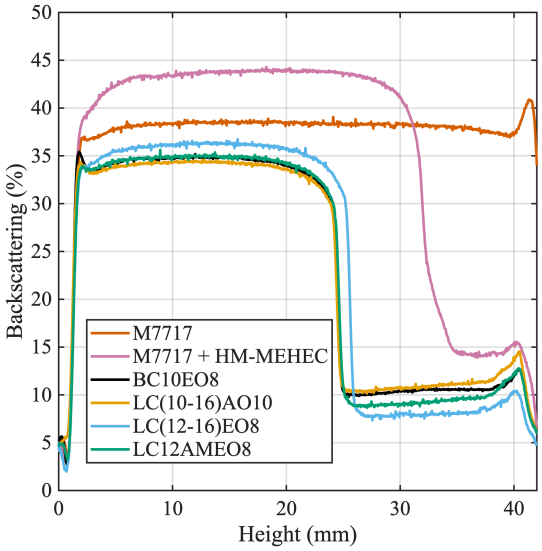
(a) 0.01 wt% of various surfactants on the day of preparation.



(b) 0.01 wt% of various surfactants two days after preparation.



(c) 0.5 wt% of various surfactants on the day of preparation.



(d) 0.5 wt% of various surfactants two days after preparation.

Figure B.1: Graphs showing BS over time of dispersions containing 20 wt% dry latex (M7717), 0.5 wt% HM-MEHEC, and various surfactants at concentrations of 0.01 and 0.5 wt%, taken on the day of preparation and two days later. Latex-only and latex–polymer dispersions are shown as references.