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CELLULOSE NANOCRYSTALS AS ‘GREEN’
EMULSIFIERS STABILIZING CRUDE OIL IN WATER
EMULSIONS

A Thesis

Presented for the M.S. in Engineering Science
with an Emphasis in Chemical Engineering Degree

The University of Mississippi

by

OMAYMA ALAZZAM

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ABSTRACT

This study examines the ability of CNC to stabilize crude o/w Pickering emulsions. The effects of concentration of CNC, ionic strength of the aqueous phase, volume fraction of crude oil to water, and the presence of divalent ions on the stability of crude o/w emulsions were examined. Emulsions stabilized with different concentrations of CNC vary from 0.1 to 1.0wt% were prepared and examined by visual assessment for creaming analysis and microscopic pictures to analyze droplet size and size distribution. Low concentration of CNC as 0.1wt% didn't help with forming stable emulsions. As the concentration of CNC stabilized the emulsions increased, the stability of emulsions over time increased because of the ability of CNC particles to fully cover and pack the oil water interface and therefore prevent coalescence. Samples were analyzed and the change in stability of emulsions upon storage was studied by analyzing microscopic pictures and by visual assessment of creaming behavior through a period of time up to 32 hours. Emulsions were prepared with different ionic strength of NaCl varying from 0.3 to 1.9M. Solutions with higher ionic strength formed more stable emulsions against coalescence by decreasing droplet diameter and the rate of growth of droplets with time. On the other hand, higher ionic strength showed faster creaming and a more creamed aqueous phase. API brine and Synthetic seawater stabilized emulsions showed less stability of emulsions due to the presence of divalent ions Ca^{2+} and Mg^{2+} , which may reduce repulsive forces between droplet and cause coalescence.

CNC has shown a great efficiency in stabilizing crude o/w emulsions. Interestingly, experiments showed that CNC should be combined with salt in order to effectively stabilize emulsions. Therefore, increasing ionic strength of aqueous phase will cause an increase in the stability of emulsions.

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1. CHAPTER ONE: INTRODUCTION

The main objective of this project is to study the ability of Cellulose Nanocrystals (CNC) for stabilizing crude o/w emulsions. Factors that affect this stability such as CNC concentration, ionic strength of water, and the presence of divalent ions were examined. In this introduction, information about crude oil and crude oil spill issues are introduced. Emulsions and Pickering emulsions, CNC, and their unique stabilizing properties are discussed.

1.1 Economic impacts of oil spills.

Oil spills are defined as the release of a liquid petroleum hydrocarbon into the environment, especially marine areas, due to human activity, and is a form of pollution. Oil is a prevalent pollutant found in oceans and its effects can be devastating for many reasons. [1] One of the most costly activities that oil spills negatively impact is tourism, which is essential for generating income and creating employment opportunities. In “The Growing Importance of Travel and Tourism to the Global Economy,” Sam Weston asserts that tourism “contributed 9.5% to the global economy, created 4.7 million new jobs and supported 266 million jobs in 2013.” [2] Oil spills disrupt many of the common coastal recreational activities such as swimming, fishing, diving and surfing.

This ocean contamination also affects the sea life as it causes seafood restaurants to close, resulting in a major loss of income. Contaminated beaches will also be closed for cleanup, this

ultimately stops all tourism in the area due to beaches being the primary source of tourism in coastal areas. [3]

Oil spills also affects the generation of power. Electric power plants condense steam from turbines through the tubular circulation of seawater. If the source of seawater is contaminated , this will cause the electric power plant to shut down and force electricity to be bought through other channels. This is a catastrophic consequence of oil spills. [2], [4] . Seawater is integral to producing salt in regions where rain fall is limited. One of the primary components of seawater is salt. The extraction occurs through the use of a salt evaporation pond. This is a pan that is engineered to extract salt from seawater. The sun and wind evaporates the water and the salt left behind is harvested. There are pans that can be cleaned if contaminated by oil in the sea water, however mud based pans cannot be cleaned as easily. The maintenance of these mud based pans will be costly, therefore negatively affecting the production of salt. [5]

Another significant negative affect of oil contamination in seawater is the strenuous cleaning that will be necessary by many fishermen to their large boats and ships. These vessels are often held in marinas and harbors.

Although less severe staining can be easily cleaned, severe staining will require vessels to be transported to other locations for a more taxing and demanding cleaning process. This problem is more prevalent with ports. [3]

1.2. Cleaning up oil spills.

Cleaning up oil spills is not an easy process. Since water has a density of 997 kg/m^3 whereas oil has a density between 870 kg/m^3 - 920 kg/m^3 [6]. When these two substances are mixed, seawater forms a layer underneath the oil layer because of its higher density. Oil separates to form a layer on the top of seawater and these results in a much easier process when it comes to cleaning up an oil spill. There are four primary methods of cleaning up oil spills: oil dispersants, booms/skimbers, sorbents and leaving the oil alone. [7]

The formation of oil dispersants is the most common method of cleaning up oil spills and this is accomplished by the behavior of surfactant molecules. Surfactants are composed of hydrophilic heads and hydrophobic tails. The hydrophilic head is attracted to the water molecule and the hydrophobic tail attaches itself to the oil molecule, thus breaking the oil down into minute droplets. Once the oil is broken down into droplets, the naturally occurring wave movement disperses the droplets into the sea and then the surfactant molecules will be consumed by the sea's bacteria. Although this method has its benefits, there are also some drawbacks. Animals in the sea will often mistake the oil droplets for food, therefore these contaminated droplets will be consumed by organisms. There is also speculation that the dispersants themselves can be as toxic as the oil contamination. [7], [8]

Another common method of oil cleanup is the use of booms and skimmers. Booms are a mechanism that prevents the oil from spreading. It contains a freeboard that is located above the surface to contain the oil, a skirt located below the surface preventing the oil from escaping and a cable to stabilize the boom. In order to effectively store the oil, barges are

placed throughout the ocean. This method works more effectively for smaller oil spills because skimmers can get clogged easily. [7]

Sorbents are also useful in oil spill cleanup. The use of sorbents is accomplished through absorption and adsorption. Because oil often forms a liquid layer on specific materials, the use sorbents are effective in its removal.

A drawback of this method is that it is effective on the surface of the water and cannot effectively remove oil from materials that become heavier than water and sink to the bottom, thus exposing organisms in the sea to these oil particles. [9]

Some scientists argue that an oil spill should be left alone and allowed to disperse naturally. They argue that the natural movement of the sea and wind will result in the oil dispersing naturally.

This is true for high energy environments, but this is not the case for low energy environments. In a low energy environment, oil will not be eliminated, but will continue to exist for a long period of time. [10]

1.3. Crude oil definition and composition.

Crude oil is a naturally occurring substance found in the earth composed of hydrocarbons and other organic compounds. It is often found deep in the earth and recovered by drilling wells to access the oil deposits. The crude oil is then refined by fractional distillation to make various petroleum products. The process to refine the crude oil is based on its chemical composition.

The chemical components of crude oil generally belong to one of several classes of compounds. These include large and small aromatics, large and small saturates, resins, and asphaltenes. All aromatics have at least one benzene ring in their chemical structure; small aromatics have one or two rings while large aromatics have additional benzene rings. Small aromatics are mostly water soluble while larger aromatics are not. Saturates are alkanes which come in multiple forms, including aliphatic with the structure of C_nH_{2n+2} , and alicyclic with the structure C_nH_{2n} (also known as cyclic saturates.) Small saturates are highly dispersible and evaporate quickly while large saturates, which include waxes, cause dispersion, anomalous evaporation, and emulsification. Waxes are generally straight-chain saturates and have a melting point above 20°C. Resins and asphaltenes are very similar compounds, with asphaltenes having a structure comparable to large resins. Both resins and asphaltenes contain condensed aromatic nuclei carrying alicyclic and alkyl systems with heteroatoms including oxygen, nitrogen, and sulfur. Asphaltenes may also contain metals such as iron, nickel, or vanadium. Neither resins nor asphaltenes evaporate, degrade, or disperse noticeably and they are both able to stabilize emulsions of water and oil when the concentration is >3%.

The chemical composition of crude oil is extremely complex, which can render these definitions too simplistic to be greatly beneficial. Various techniques can be used to develop a better understanding of the chemical nature of different components of crude oil. High pressure liquid chromatography (HPLC), open column chromatography, and thin-layer chromatography with flame ionization detection (TLC-FID) are all techniques used to determine aromatic, saturate, and polar content of the crude oil; however, each technique is likely to provide a

different result, and TLC-FID is generally not used for fresh oils because of the loss of low-boiling components.

Various methods are used to determine the hydrocarbon groups in crude oils. First, asphaltene can be precipitated from n-pentane. Then the oil without asphaltene can be placed on an open silica column and sequentially eluted with solvents of increasing polarity to separate the aromatics, saturates, and resins. There are multiple ways to determine the wax content. One method (used for very waxy or viscous oils) analyzes the saturate fraction using gas chromatography with flame ionization detection. Another method is to use a mixture of methyl ethyl ketone and dichloromethane at -32°C to precipitate the waxes from the maltenes. For oils with an initial boiling point over 250°C , it is possible to obtain a good mass balance ($>95\%$). In oils with an initial boiling point $<250^{\circ}\text{C}$, light ends can be lost during the solvent recovery process resulting in poor mass balance. These methods still allow calculation of the distribution of hydrocarbon groups in the oil, assuming that 1) the aromatic portion of the lost light ends is equal to the total volatile organic compounds, and 2) asphaltene and resin contents are not affected by the losses due to evaporation. [11].

1.4 Emulsions in petroleum production

There are three types of emulsions that form in crude oil production, w/o emulsions, o/w emulsions, and multiple/complex emulsions. The most common type of emulsions encountered is water-in-oil emulsions. These consist of tiny droplets of water suspended in a continuous oil phase. Emulsions occur because oil is generally co-mingled with water, and while some of it may settle out quickly, the rest is trapped in the oil in the form of an emulsion.

The properties of these emulsions vary based on numerous factors, including droplet size, liquid phase viscosity, liquid densities, temperature and interfacial tension. [11], [12]

Emulsions create technical challenges because they change the properties of the oil. The viscosity of emulsions is generally higher than that of either water or oil, as a result of the suspended droplets, and they can show non-Newtonian shear-thinning properties as well. They can interfere in a number of ways with petroleum production by creating high pressure drops in flow-lines, causing the production of off-specification oil, and trip separation equipment in gas and oil separation plants. [10]

1.5 Asphaltene stabilizing properties

It is generally accepted that resins and asphaltenes are the primary components responsible for the stabilization of o/W emulsions, although naphthenic acids and fine solids may also be contributing factors. For any particle to play a role in emulsion stabilization it must be present at the oil/water interface and be wetted by both the oil and the water. However, there is some debate on the exact method by which asphaltenes stabilize the emulsions. Because of their surface-active properties, asphaltenes stay at the oil/water interface and create a rigid film, preventing the water droplets from coalescing. Even the state of the asphaltenes has an effect on the stabilization of emulsions; not-yet-flocculated asphaltenes in a colloidal state can stabilize emulsions, but precipitated asphaltenes in the solid phase have significantly stronger stabilization properties. [11]

Pressure, solubility, and organic dispersants all affect the chemistry of asphaltenes. Decreasing pressure approaching the bubble point results in light components such as methane and ethane occupying significantly more volume compared to other components, which leads to a change in the solubility parameters of the fluid. This can cause flocculation or precipitation of asphaltene. Below the bubble point, the light components form a gas phase and further reduction of the pressure will reduce the influence of the light components on the solubility, which might have the effect of making the asphaltene aggregates solvable again. Without efficient dispersants, precipitation occurs on a large scale, while dispersants will cause the small particles of asphaltene to become suspended in the oil. [11], [6].

1.6 Emulsions

An emulsion is a particular type of colloid that consists of droplets of one liquid phase dispersed in another liquid phase, where the two liquids are immiscible. They are by their nature thermodynamically unstable systems. The dispersed phase is the droplets, which are suspended in the continuous phase. Oil and water commonly form emulsions, either oil-in-water, or water-in-oil. Emulsions of oil and water generally separate rapidly due to the molecular incompatibility of the two substances. This significantly reduces the contact area between the phases and thereby reduces the free energy of the system as well. To prevent this rapid separation, emulsion stabilizers may be used. [13]

Derjaguin-Landau- Verwey-Overbeek (DLVO) theory explains the stability of colloids by describing the interactions between charged surfaces of dispersed particles.

It argues that there are two main types of forces between particles, electrostatic repulsion and van der Wall attraction. The balance between these energies is quantified referring to DLVO theory and expressed by the mean of total potential as shown in the equation below [14]:

$$V^{tot} = V^{el} + V^{vdw} \dots\dots\dots(1)$$

According to equation 1, the total potential between colloids is the summation of the potentials accounting for both electrostatic repulsion V^{el} and van der Waals attraction V^{vdw} .

More specifically, the electrostatic repulsion potential between two planes that are separated by distance d [m] is given by [15]:

$$V^{el}(d) = \frac{64n_b k_b T}{\kappa} \exp(-\kappa d) \dots\dots\dots(2)$$

And the potential that accounting for van der Waals interaction is given by:

$$V^{vdw}(d) = -\frac{A}{12\pi d^2} \dots\dots\dots(3)$$

Where the inverse of κ [m] is the Debye length, n_b is the bulk concentration of the electrolytes, A [J] the Haymaker constant, T is temperature [K], and κ_b is the Boltzmann constant. [15] Note that this expression concerns two interacting planes but the trend is the same for all other cases such as for spherical shape.

There are two common types of stabilizers used to maintain emulsions. Thickening agents can be used as stabilizers in some emulsions; by increasing the viscosity of the continuous phase, these stabilizers reduce the speed at which the droplets settle out of the dispersion and

slow down the coalescence and flocculation of the droplets. Thickening agents are commonly used as stabilizers in oil-in-water emulsions, particularly in food applications, and include hydrocolloids such as xanthan gum [16].

The other type of stabilizers, known as emulsifiers, is made up of amphiphilic molecules, which, because of their molecular structure, have affinity for both polar and non-polar media. These molecules are surface active and lower the free energy of the system by reducing the interfacial tension. They are used to kinetically stabilize emulsions and prevent or delay phase separation. Emulsifiers include various biopolymers as well as surfactants. [17], [18].

Surfactants are performance chemicals in that they are used to perform a specific function in a product or process, unlike other chemicals which are used in the course of a reaction to produce a product or another chemical. Surfactants lower interfacial tensions between two chemicals, often two liquids, such as oil or water, but they can be used between a gas and a liquid or a solid and a liquid as well. Because of their chemical nature, surfactants are effective emulsifiers, and can be used as dispersants, wetting agents, and detergents. [17] One particular concern when it comes to surfactants is their impact on the environment, especially biodegradability and potential toxicity to marine life. Many studies have been conducted to determine the impact that surfactants have on the environment, particularly where marine organisms are concerned. The primary factors influencing the chemicals' toxicity are the tendency to adsorb onto the organisms and the ability of the chemicals to penetrate cell membranes. Additionally, some studies have shown that higher biodegradability also correlates with higher toxicity to marine organisms. [19], [7]

1.7 Pickering Emulsions

Pickering emulsions are a specific type of emulsion stabilized using solid particles instead of other methods such as surfactants, and use a different method to stabilize the emulsion than conventional emulsions stabilizers. In this method, the solid particles are partially wetted by both oil and water and position at the o/w surface based on the affinity for each phase [20], [17]. Discovered at the beginning of the twentieth century by Ramsden and S.U. Pickering [21], they did not become widely studied until the 1980s. Since then, they have become widely used in a number of applications, including biomedical applications, food products, and cosmetics. Examples of Pickering emulsions include “dry water,” a water-air emulsion stabilized by adsorbed silica particles, marketed by The Degussa Company in 2004, as well as various applications in food products. Crude oil is another area where Pickering emulsions receive significant attention in the scientific literature. Crude oil is a water-in-oil Pickering emulsion stabilized by surfactants such as maltenes, as well as adsorbed solid particles, including asphaltenes. [10] This presents significant difficulties in demulsifying crude oil which has received significant attention and scientific efforts [6].

Pickering emulsions show some definite advantages over emulsions stabilized by other methods, including surfactants [17]; however, they do still retain the properties of classical emulsions and can, in fact, be substituted for classical emulsions in many applications. The stability of Pickering emulsions is superior due to the formation of a densely packed layer of particles at the droplet surface. This layer creates a mechanical barrier that prevents the coalescence of the droplets, thus stabilizing the emulsion [17]. Because of Pickering emulsions chemical structure, a high level of energy is required to remove these solid particles from the

interface, meaning that they will not be removed spontaneously once they are in place at the oil-water surface [20]. In addition, the number of particles needed is much smaller than with traditional stabilizers. However, small changes in environmental factors, chemical composition of the particles or the emulsion chemicals, can cause much larger changes in stability [20].

The various physical and chemical aspects as well as the stability of the emulsions are very important to chemical processing and the development of new products. The particles used to stabilize the emulsion are of course smaller than the droplets in the emulsion [22]. By using extremely small, nanometric size particles, the droplets may be quite small as well, sometimes only a few microns in diameter. On the other hand, larger particles can in turn stabilize larger droplets, even reaching the size of a few millimeters in diameter, something that is not generally possible with classical emulsions [22], [23]. Conventional Pickering emulsions are based on the formation of a densely-packed barrier of particles that forms at the oil-water interface, and the strength of this barrier is determined by the amount of energy required to remove the particles from the surface of the droplets. [24], [21] [25].

Inorganic particles ranging in size from nanometers to micrometers, including silica, clay, montmorillonite, graphite, calcium carbonate, and polystyrene can all be used for various applications.

Often, the nanocrystals in their natural state tend to aggregate and do not show the hydrophobic/hydrophilic tendency needed to act as a stabilizer in Pickering emulsions; these particles require surface treatment in order to become effective emulsifiers. Various methods have been developed to modify the particles, including methods that add surfactants and those

which modify only the surface of the particle to make it fit the desired purpose. Another option for Pickering emulsifiers does not require the particles to be amphiphilic [26].

Particles with partial wettability in both oil and water can serve as stabilizers because of their tendency to partition preferentially at the oil-water interface. The stability of emulsions with these compounds depends on the size and shape of the particles, as well as their wettability, concentration, and tendency toward particle aggregation. However, if the particles show complete wettability, they will not form an emulsion and instead will be suspended in one phase or the other [27].

1.8 Biocompatible organic compounds

In addition to inorganic particles, biocompatible organic compounds such as chitin [28], bacteria [24], starch [29] and cellulose [30] can be used as Pickering emulsifiers. Among the organic compounds used for this purpose are cellulose fibrils, microcrystalline cellulose, CNC, and cellulose derivatives. These include compounds derived from various sources, including bacterial cellulose and silylated micro- and nanocrystals fibrils from wood pulp, which have been demonstrated to be effective for stabilizing Pickering emulsions [30].

Cellulose specifically has the advantage of being widely available, renewable, and easily modified when needed using strong-acid hydrolysis to create additional particles with unique properties and new applications. These compounds generally have the advantage of being non-toxic and biocompatible [20], and different compounds have different strengths and weaknesses. For example, fibrillated cellulose has a high aspect ratio and tends to produce droplet networks

rather than individual droplets in the emulsion. Shorter cellulose fibers, such as CNC, are more suitable for controlled interfacial stabilization because they form a denser layer on the surface of the droplets [23].

As mentioned before, the small solid particles used as Pickering emulsifiers require very high energy to remove from their place on the oil-water interface, when compared with other emulsion stabilizers. By using polymer grafts that respond to environmental changes, these organic particles can then be used to control the stability of Pickering emulsions [29].

1.9 CNC as Pickering Emulsifiers

CNC are a type of organic particle from cellulose produced by sulfuric acid hydrolysis that have unique properties which make them effective as Pickering emulsifiers [31]. Research on CNC is still in the early stages, but eventually they may prove to be one of the most desirable stabilizers for Pickering emulsions, when all aspects such as cost, availability, and environmental impact are considered and they are a better option for many applications than inorganic particles [25] [26] [23].

One small disadvantage is that cellulose particles are globally hydrophilic (although they have hydrophobic edges [20]). Meaning that surface modifications are often required to improve their efficiency as stabilizers for o/w emulsions. However, cellulose particles have been shown to be effective for even long-term stabilization of Pickering emulsions [20].

In addition, the hydrophobicity of CNC, and thus potentially the effectiveness of the emulsifier, can be increased by adding chemicals such as alkyl amines or silanes [32] which aid in the stabilization. This process usually requires multiple steps and involves modification of the particle surface. However, these processes are not always suitable in all applications because they can affect the chemistry of the resulting emulsions [26].

Another method for modifying the CNC is to use a combination of surfactants and CNC to stabilize emulsions [17]. This allows greater control over the emulsion properties, and the use of CNC allows for less surfactant to be used, which is considered desirable due to the environmental concerns associated with surfactant uses. Natural amphiphilic molecules and biocompatible surface-active polymers are other lower-toxicity options available for stabilizing emulsions alongside CNC [20], [17].

1.10 CNC properties and advantages.

CNC is new, commercially available nanoparticles derived from natural cellulose. They have recently become a point of interest for research because of their unique properties, such as high aspect ratio, biodegradability, biocompatibility, high surface activity, and being environmentally friendly Advantages [23], [33], [28].

CNC have recently been demonstrated to stabilize emulsions, and because of their “green” nature and non-toxicity, CNC show promise as emulsifiers, stabilizers and gelation agents in products as diverse as pharmaceuticals, cleaning supplies, personal care products, and even foods [25]. The intermediate wettability and nonmetric size of CNC allows them to adsorb at o/w interfaces [26].

Cellulose is widely available; as the most abundant renewable organic material in the entire biosphere it is distributed widely in plants and certain marine animals, and less widely in other organisms including fungi, bacteria, and algae. First isolated by Anselme Payen [33] in 1838, cellulose is a tough, fibrous substance that is insoluble in water and is responsible for the rigid structure of plant cell walls. Since its discovery, cellulose has been extensively studied for its physical and chemical properties and new discoveries are always being made. Because of their stiffness, high strength, biodegradability, and low weight, combined with their abundant availability, polysaccharide nanocrystals show promise as candidates for many applications in the field of material science [23], [33], [28]. The safety of natural nanocrystals is an obvious and important concern in the development of CNC, which at this time have been found to have low potential for toxicity and environmental risk and shows no harm to aquatic organisms [30], [20]. It is biocompatible and biodegradable and has potential for novel biomedical nanomaterials for cellular Nano scaffolds, cellular bio imaging materials, and instant drug delivery. There has been much interest in the use of CNC composites because of the focus on the use of renewable resources.

The geometric dimensions of CNC vary based on the source and extracting methods [22]. For CNC derived from wood, the CNC are generally between 5-10 nm in width and 100-300 nm in length. CNC with a rod-like morphology are generally derived from botanic sources such as cotton or flax. Their length ranges from 100 nm to 700 nm, and their diameter from 5 nm to 30 nm. CNC from bacterial cellulose have a length ranging from 100 nm to several mm, and diameter from about 5 nm to 50 nm. The preparation of spherical CNC has also been reported. Starch nanocrystals with a platelet-like shape are derived from crops such as peas, potatoes, and

corn. These have a length of 20–100 nm, a width of around 25–30 nm and a thickness of 6–8 nm [34]. The distribution, size, and shape of polysaccharide nanocrystals can be investigated using a variety of methods, including atomic force microscopy (AFM), transmission electron microscopy (TEM), atomic force microscopy (AFM) and field-emission scanning electron microscopy (FE-SEM) [23] .

CNC are derived from the crystalline components in various cellulosic materials. The crystalline structure controls the stiffness of the various CNC, and there have been investigations on calculating the theoretical stiffness of using elastic modulus values in the range of 120-170 GPa [23]. Both the X-ray diffraction technique and Raman spectroscopic technique have been used to measure the stiffness of CNC, delivering results of 138 GPa and 143 GPa respectively. [33].

The crystalline structure of CNC is determined by the ordered packing of polysaccharide chains. Intermolecular hydrogen bonds and van der Waals forces between oxygens and hydroxyl groups of adjacent molecules promote parallel stacking of multiple polysaccharide chains forming a crystalline structure during biosynthesis. Crystallinity values for starch nanocrystals range from 45-50% and from 54-88% for CNC [33].

CNC can be considered rigid rods due to their high aspect ratio and stiffness. Because of this, nematic behavior can be expected under certain conditions. The helical twist along the main axis of cellulose crystallites can cause crystal suspensions to form a helical twist normal to the main axis of the rod. This organizes them into a nematic phase or cholesteric phase of stacked planes aligned on a perpendicular axis.

The liquid crystallinity, domain size, pitch, and ordering as well as other properties can be affected by factors including shape and size, dispersity, charge, ionic strength of the solution, and external stimuli. Various factors such as size, shape, dispersity, charge, ionic strength of the solution (electrolyte), and external stimuli can affect the liquid crystallinity, pitch, domain size, ordering, and other properties. In addition, the rheological properties and phase behavior of cellulose nanocrystal suspensions are believed to correspond to both the concentration and the temperature [25].

Acid hydrolysis of cellulose is a chemical process that uses a strong acid, such as sulfuric or hydrochloric acid, to isolate the CNC and remove the amorphous region.

This process results in negatively charged surface acid groups which promote homogenous dispersion of oil in water by inducing the electrostatic stabilization of the nanocrystals, and the dispersion state of the CNC will determine their application and properties [31]. The dispersion state includes the interfacial interaction between the CNC and the matrix molecules in composite materials as well as the surface modification process. In most organic solvents CNC aggregate as a result of strong inter-particle hydrogen bonding, due to their high surface area and hydrophilic nature [16]. Hydrolysis results in negatively charged surface acid groups on polysaccharide nanocrystals when sulfuric acid is used as the hydrolyzing agent. These groups promote homogenous dispersion by inducing the electrostatic stabilization of the nanocrystals. In this way, the interparticle hydrogen bonding can be weakened using surface chemical modification. In high ionic strength aqueous solutions, the CNC also aggregate, due to the screening of electrostatic repulsive forces [16], [26], [23].

Cellulose materials have been reported to stabilize both w/o emulsions and o/w emulsions using hydrophobized microfibrillated cellulose (MFC). However, these fibers have the drawback of aggregation, the presence of contaminants, and the fact that their length cannot be controlled, which in turn makes it difficult to control important emulsion characteristics such as drop size, viscosity, and reproducibility. Such highly controlled conditions can only be obtained using small, well-defined particles [29]. These highly crystalline particles of varying morphology can be prepared using acid hydrolysis.

Acid hydrolysis processing conditions such as acid concentration, time, temperature, and the purity of the material, as well as the origin of the cellulose can affect the surface chemistry. Because unmodified cellulose is hydrophilic with hydrophobic edges, it can only stabilize o/w emulsions, hydrophobic modifications are required to stabilize water-in-oil emulsions.

The surface of CNC is reactive and covered in active hydroxyl groups, which provide the possibility for numerous chemical modifications. Usually, the purpose for the chemical modifications is to create polysaccharide nanocrystals that can contribute to specific functions in nanomaterials or are available to be used as reinforcement in composite materials. The content of the active hydroxyl groups on the surface of CNC can be calculated from their molecular structure in rod-like CNC with uniform geometric dimensions [33].

The many hydroxyl groups on the surface of CNC provide an advantage which allows for various modifications. Attempts have been made at esterification, sialylation, polymer grafting, and oxidation [26]. In addition, there have been studies on surface modification, including polymer coating and using adsorbing surfactants.

Grafting thermo-responsive polymers to CNC is another example of a surface modification conducted on CNC which has been used to control the hydrophobicity with temperature. There are two main reasons for conducting surface modifications of CNC. One is to induce better dispersion by creating stable negative or positive electrostatic charges on the surface. The other is to modify the surface energy characteristics to improve compatibility when used with hydrophobic or non-polar matrices in nanocomposites. When conducting chemical modifications on the surface of CNC, the primary challenge arises from the difficulty of modifying only the surface while maintaining the original morphology, avoiding polymorphic conversion, and preserving the integrity of the crystal [26].

The use of CNC to stabilize water-in-oil emulsions requires surface modifications to obtain sufficient amphiphilicity due to the hydrophilic nature of cellulose surfaces. On the other hand, microcrystalline CNC can stabilize oil-in-water emulsions without surface modification, through the formation of networks around the oil droplets [34].

Various studies have shown the potential for stabilizing oil-in-water Pickering emulsions and foams using microparticles of hydrophobic cellulose, including unmodified bacterial cellulose, bacterial CNC, and fibrillated cellulose.

Other studies have been done on the use of cellulose from silylated micro- and Nano fibrils from wood and bacterial sources in the stabilization of water-in-oil emulsions [20].

2. CHAPTER 2: CNC STABILIZED EMULSIONS OF CRUDE OIL IN SEAWATER AND BRINE SOLUTIONS

2.1 Motivation

In the previous chapter, emulsions and Pickering emulsions were described. The role of solid nanoparticles on the stabilization of emulsions was also discussed. In the case of cleaning up oceans and seas; non-toxic dispersant must be considered because toxic compounds harm marine life and affect organisms. Also cleaned water may be used for agriculture. For these reasons, biomaterials are of interest for cleaning up oil spills, and CNC was studied due to its unique properties.

In this chapter, experiments were performed to examine the stabilizing properties of CNC for crude o/w emulsions while varying factors such as concentration of CNC, ionic strength of water, and the presence of divalent ions.

2.2 Experimental Section

2.2.1 Materials and methods

CNC (11.5 wt.%), prepared from wood pulp, made by the USDA Forest Products Laboratory and distributed by The University of Maine were used as received. Calcium chloride (CaCl_2), sodium chloride (NaCl) and synthetic seawater (SSW) were all purchased from Sigma. Crude oil was kindly supplied by Valero refinery Memphis TN.

2.2.2 Preparation of emulsions

Various concentrations of CNC (0.2, 0.8, 1.9, and 2% wt.) were prepared by diluting the CNC stock 11.5% w/w using distilled water. Emulsions were prepared by mixing equal volume of CNC with aqueous solutions having different ionic strength. These solutions are 200% API brine, 200% SSW, different ionic strengths of NaCl solutions (0.60, 1.12, 1.9, and 3.8 M). Emulsions with different volume fractions of crude oil to water (5%, 10%, 20%, 25%, and 50% o/w) were prepared by first adding drop by drop of the salt solutions to a CNC dispersion while mixing using a high shear mixer (IKA Ultra Turraz T-25). Different volumes of crude oil were then added to the resulting homogeneous aqueous phases. A total of 4 min of mixing time was used; 2 min for homogenizing the aqueous phases, followed by 2 min while adding crude oil drops. The rate of mixing used did not exceed 12000 rpm to prevent splashing the sample. Gentle mixing was sufficient to allow the formation of micrometric-sized droplets and to assist forming stable emulsions.

To avoid introducing air bubbles into the emulsions, the tip of the mixer was placed halfway from the bottom of the vial into the solution during mixing. Emulsions were prepared in 8.5 cm height tubes and the tubes were sealed and stored at room temperature.

2.2.3 Conductivity measurements

Orion DuraProbe 4 electrode conductivity cell was used to measure the conductivity of the emulsions. Measurements were taken immediately after shear mixing and 24 hours after storage to examine the type of the emulsions.

In general, high conductivity indicated o/w emulsions and low conductivity ($<5 \mu\text{S/m}$) indicated w/o emulsions. If the conductivity changed significantly after a period of storage time, a phase inversion occurred.

2.2.4 Visual assessment of creaming.

Visual appearance of the emulsions with time was analyzed immediately after shear mixing. Tubes were set in front of camera at room temperature and the separation of the emulsion from the aqueous phase was tracked by taking pictures every hour and examining the movement of the creaming front. Creaming is commonly referred to as gravitational separation and is the process whereby droplets separate and move upward due to a higher density of the aqueous phase.

Creaming rate was calculated by measuring the change in the creamed layer height (H_c) versus the total emulsion height upon time. The following relation of creaming index characterizes the extent of creaming:

$$\text{CI (\%)} = \frac{H_s}{H_t} * 100 \dots\dots\dots (4)$$

Where CI is the creaming index, H_s is the serum layer height and H_t is the total emulsion height.

2.2.5 Droplets size and droplets size distribution

Emulsion droplets were visualized using an optical microscope (Amscope 500MD). A drop of the emulsion was directly applied onto a glass microscope slide and covered with a glass cover slip without putting pressure on it in order to avoid droplets damage or coalescence.

Pictures were viewed under a magnification of 120X to 160X.

Droplets diameters for almost 150 oil droplets were measured using ImageJ software. The average diameters and size distributions were calculated for each microscopic picture. Two different microscopic pictures taken from two different repetitions were analyzed for each sample.

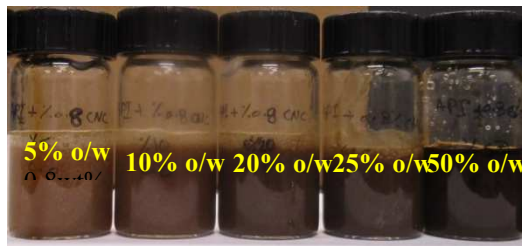
2.3 Results and Discussion

2.3.1 Type of emulsion

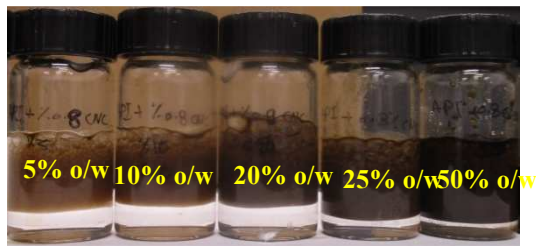
Conductivity measurements were carried out in order to determine external and internal phases of the emulsions. Measurements were taken for all different emulsions prepared using different aqueous phases. Generally, a high conductivity indicates an o/w emulsion and a low conductivity ($<5 \mu\text{S}/\text{cm}$) is indicative of a w/o emulsion [17]. Results showed significantly high conductivity values for all samples including all oil to water volume fractions. This verifies having o/w emulsions. Measurements were also taken after 24 hours to check if phase inversion occurred upon 24 hours of storage.

Results show that conductivity measurements decreased over time due to the creaming of the aqueous phase to form an eluted layer at the bottom of the tubes (see Fig.1), while the emulsion had fewer amount of ions and higher oil to water volume fraction, leading to less conductive samples. Although conductivity decreased over time, it was still significantly high and the emulsion's phases were not inverted. Fig.2 illustrates the fact that emulsions were o/w phase since the conductivity vs. aqueous phase volume fraction follows a linear trend line [35].

All the other emulsion conductivity relationships showed the same behavior with a small variation of conductivity values due to the difference of CNC concentration and ionic strength. This verifies that all emulsions were in o/w phase.



0.8wt% CNC+ API brine at zero time



0.8wt% CNC+ API brine after 24 hours

Fig.1: emulsions with different o/w volume fractions a) a zero time and b) after 24 hours of preparation

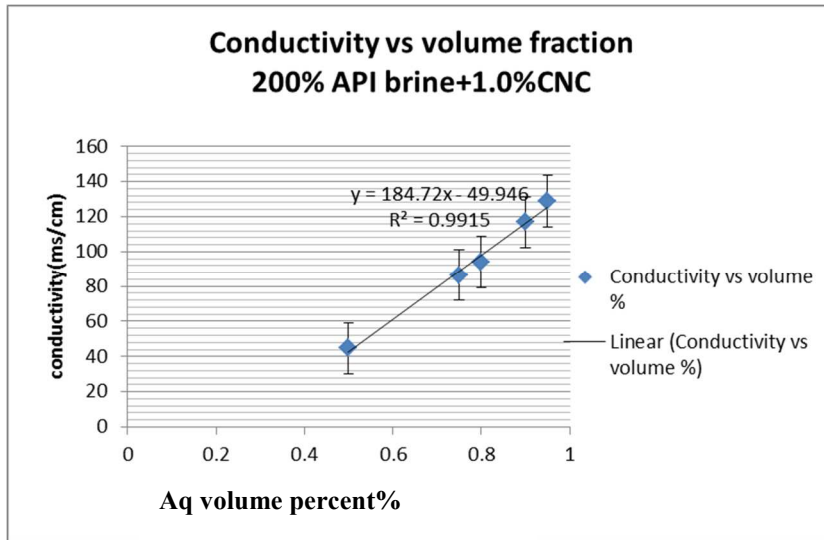


Fig.2: linear relation between changes on conductivity with different aqueous volume percent.

2.3.2 Effect of CNC concentration on the stability of the emulsion

The colloids stability is controlled by attraction and repulsion forces between particles. SSW and API brine were used with CNC for stabilizing crude o/w emulsions; Debye length values for SSW and API brine are very low as 3.82×10^{-10} [m] and 2.24×10^{-10} [m] respectively [36]. When these values are substituted in equation (2), this will give a very low repulsion potential. This means the repulsion will be screened. For an electrolyte solution containing free charges, all electrostatic fields become screened due to the polarization of these charges [37]. When the ionic strength of solution increases, this will cause a compression in the electrical double layer so the repulsive forces start to decrease and the energy barriers between particles decrease.

This result suggests that in our study using a high salt concentration, stability of emulsions is not controlled by electrostatic forces, so the DLVO theory is not useful in calculating and examining stability of droplets to coagulate. Other crucial forces between droplets that affect stability of emulsions might be ionic binding of salt ions, hydration, osmotic pressure, and steric stability. [14], [30], [21].

The ability of emulsions to maintain consistent physical and chemical properties over time is known as emulsion stability. It is integral to understand the mechanisms that cause the instability of emulsions that may occur over time in order to explore effective ways to maintain stability. One of the most common indicators of physical instability is creaming. Instability mechanisms are connected with each other. For example, the gravitational separation of the emulsion and the aqueous phase causes the droplets to be closer to each other making them more likely to coalesce, or flocculate. This can sometimes cause additional creaming.

Creaming gives an indication about the extent of droplets aggregation, the more aggregation that occurs causes a faster creaming.

To illustrate how changing the concentration of CNC affects the stability of the emulsions upon storage, aqueous phase with a total volume of 9.5mL (which makes 95% volume fraction of w/o) was prepared by mixing 1:1 volume ratio of 200% API brine and different concentrations of CNC vary from (0.8, 1.6, and 2wt% CNC). The final concentrations of CNC after mixing are (0.4, 0.8, and 1wt%). All data reported in this thesis are for the final concentrations 0.5mL of crude oil was added to the aqueous phase and mixed thoroughly.

Phase separation was analyzed by calculating the creaming index for different emulsions. Emulsions were stored at room temperature and tubes were sealed in order to avoid evaporation and contamination.

Pictures were taken up to 32 hours after shear mixing and the fraction of the eluted layer on the bottom to the total height was calculated. Fig.3 shows how the creaming index of different emulsions stabilized by different CNC concentrations changed with time of storage. It is clear from Fig.3 and Fig.4 that emulsions stabilized with high concentration of CNC (1.0wt% .) showed slower creaming rate over time compared to those that were stabilized with a lower concentration of CNC (0.4wt% .). The fast creaming rate is due to the larger oil droplets when an insufficient amount of CNC is added to the emulsion. Ultimately, these large droplets come closer to each other and sometimes cause coalescence or flocculation.

By increasing the concentration of CNC from 0.4wt% to 1.0wt% , emulsions showed more stability against coalescence. Moreover, a lower creaming index implies limited droplets coalescence occurrence through the entire storage period.

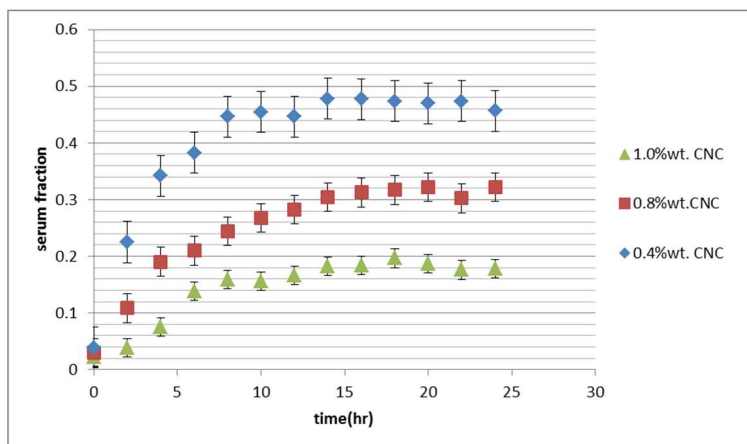


Fig.3: serum fraction vs time for 0.4, 0.8, and 1 wt. % CNC

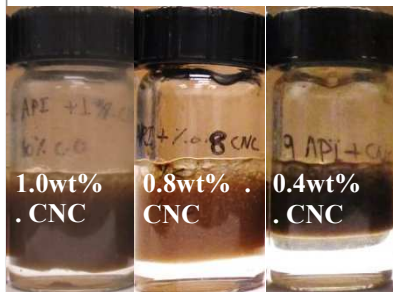


Fig.4: visual assessment of creaming after 24hrs

In order to further understand the effect of CNC concentration on the stability of the emulsions, and since the effect of creaming rate is interrelated to droplet coalescence, the droplet sizes were measured with an optical microscope. Microscopic pictures were taken of both the freshly prepared emulsions, and those after 24 hours and one month of storage (see Fig.5), to see how the droplet stability changed with time. Table 1 showed that when concentration of CNC increased, the droplets mean diameter decreased. Note that when using very low CNC concentration (0.1wt %), the two phases showed immediate separation after mixing; thus no emulsion was formed at all (see Fig.6). This indicates that the amount of CNC presented at the oil water interface was not sufficient to form uniform droplets and cover the oil water interfaces so the oil phase floated on the top of the aqueous phase.

Size in (um) vs.t	Droplets mean diameter in (um)		
Time	0.4wt % . CNC	0.8wt % .CNC	1.0wt % . CNC
At zero time	90.7	49.41	47.21
After 24 hours	82.48	56.18	49.49

Table 1: the mean droplet diameter for emulsions prepared with different CNC concentrations

Note that mean diameter might be a good indicator to compare stability, but the size distribution figures help to illustrate how many large droplets compared to small droplets the emulsion contained.. The distribution diagrams as in Fig.7 gives an indicator on how droplets change in size up to 24 hours and indicated if the emulsion had a lot of relatively large or small droplets. Having a lot of large droplets indicates that the emulsion will have coalescence and stability is not guaranteed. This might be more accurate and give a clear vision about emulsion stability.

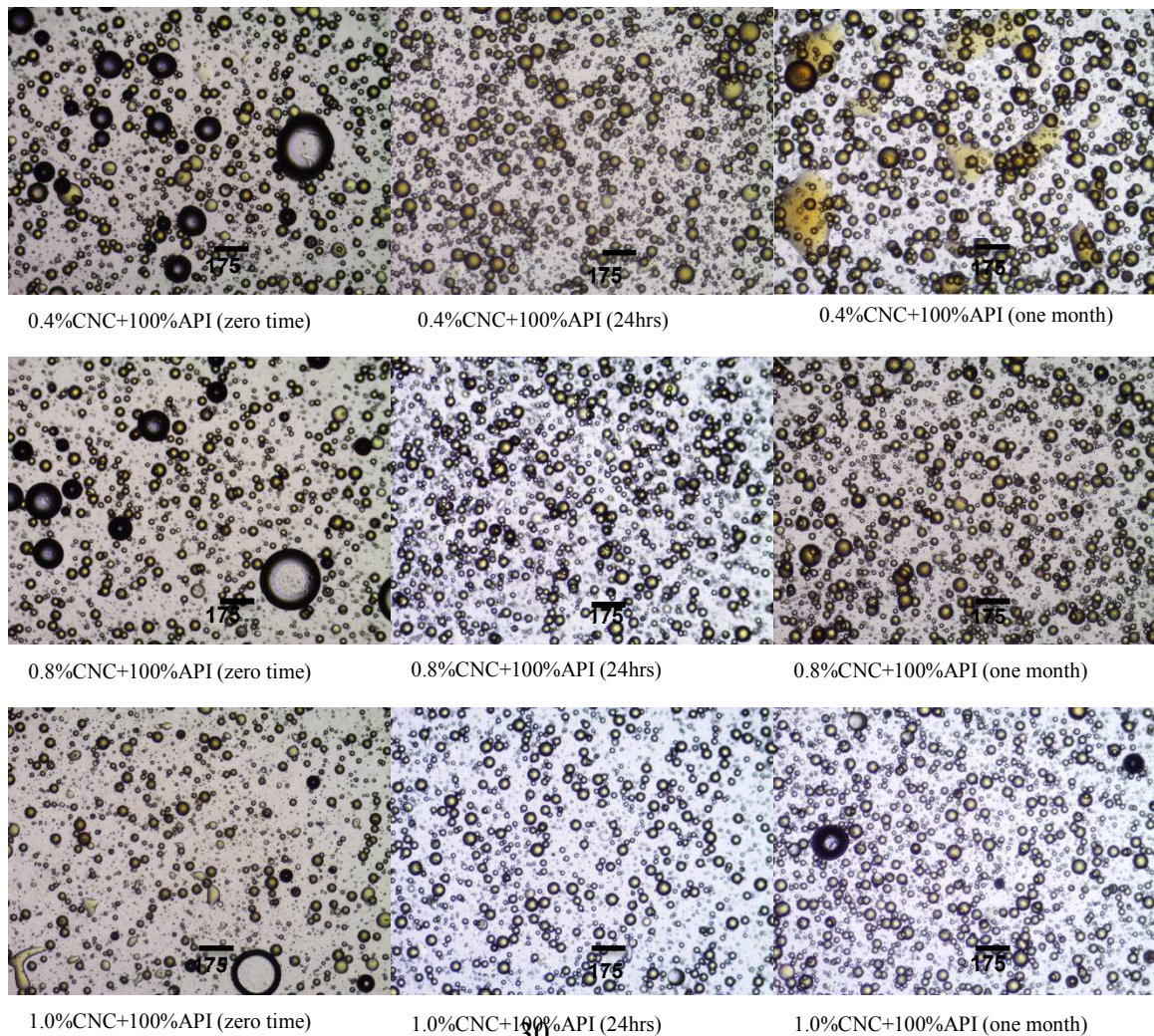


Fig.5: microscopic pictures of droplets for different CNC concentrations.

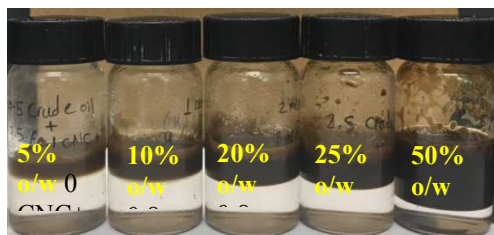


Fig.6: 0.1%CNC concentration with 200% API brine didn't stabilize emulsions.

The droplet size distribution at zero time and up to 24 hours is reported in Fig.7 a, b, and c. It is observed that droplets with a variety of different sizes experienced an increase in diameter after 24 h of storage.

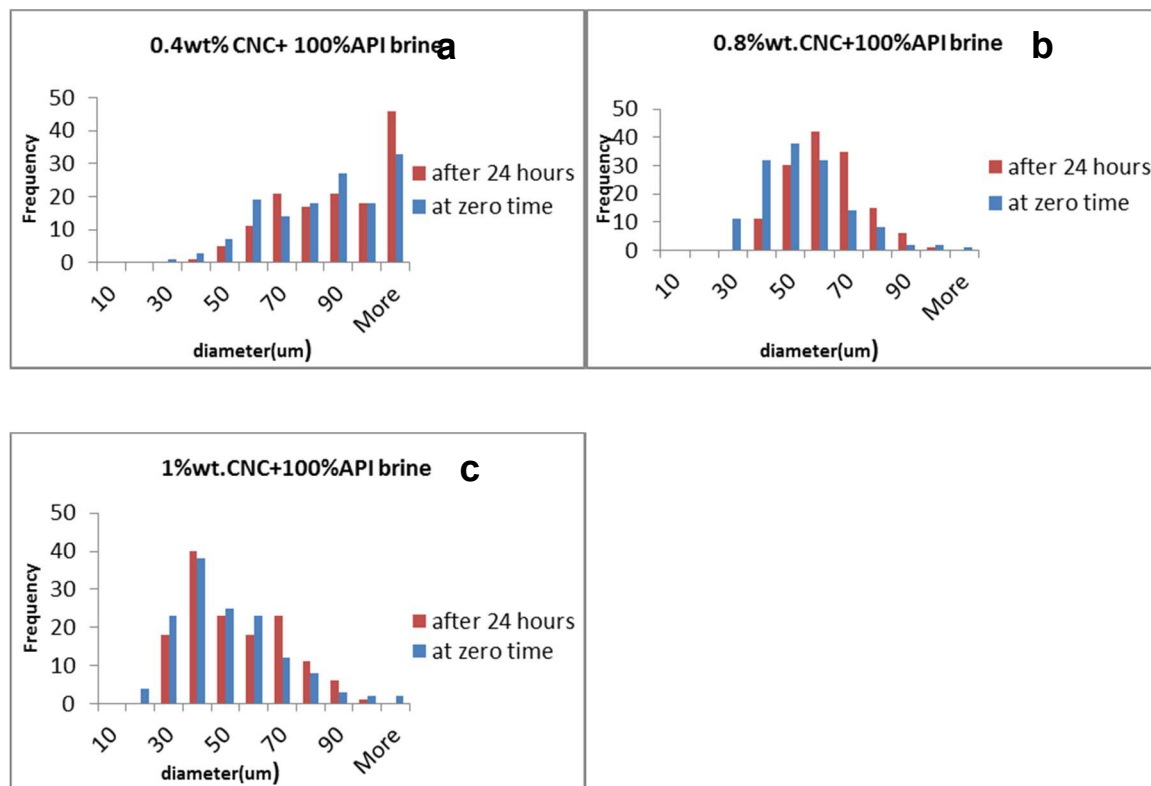
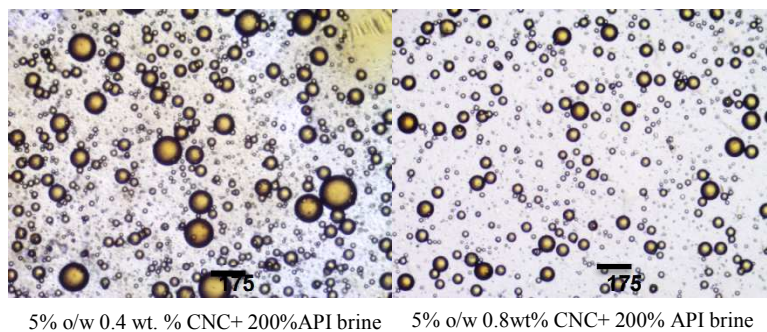


Fig.7: Droplets size distribution for emulsions with different CNC concentrations (0.4, 0.8, and 1.0 % respectively) .

Results further emphasize the fact that stabilizing emulsions with low concentration of CNC will not afford sufficient amount of CNC to cover the oil-water interface. Therefore the droplets start growing early after shear mixing and keep growing and coming closer to each other until coalescence occurs. The presence of a sufficient amount of CNC in the aqueous phase promotes formation a rigid layer around oil droplets which prevents droplet coalescence and hence forms a stable emulsion for an extended period of time.

Microscopic pictures were taken up to 6 months of storing emulsions at room temperature (Pics4a and b). Pictures indicate that when low concentration of CNC was used, after a long period of time up to 6 months, some of the droplets broke and formed larger spots of oil. The large oil droplets broke and the small ones had a significant increase in diameter. On the other hand, 1.0 wt. % of CNC was efficient in keeping droplets stable and relatively small after a long period of time, up to 6 months.



5% o/w 0.4 wt. % CNC+ 200%API brine 5% o/w 0.8wt% CNC+ 200% API brine

Fig.8: microscopic pictures of droplets for emulsions with different CNC concentrations after six months

This result confirmed past studies which found that in the case of Pickering emulsion systems, the droplet size decreases with increasing particle concentration as more particles are available to stabilize smaller droplets, and a larger interfacial area can be covered by the stabilizers. [21]

2.3.3 Droplets surface coverage

It is important to know the critical CNC concentration that needs to be used in order to sufficiently cover the droplet surface, keeping them well packed and therefore stable to coalescence. The existence of some free aggregate CNC in the bulk may be sufficient for increased emulsions stability by hindering aggregation of droplets and preventing coalescence.

The ratio of the theoretical maximum projected surface area of droplets to the actual total surface area is calculated to express the percentage of droplets surface area that is fully covered by CNC. See equation [27] (4):

$$C = \frac{mD}{6h\nu\rho} \dots\dots\dots (4)$$

Where m is the total mass of CNC, D is the mean droplets diameter, h is the thickness of CNC crystals which equals to (7nm), ρ is the density of CNC which is approximately 1.59g/cm³ and ν is the actual volume of crude oil used for preparing emulsions. [36]

The surface coverage of droplets was calculated for different CNC concentrations (0.4, 0.8 and 1wt%), and values found were 107, 108, and 146 respectively. So there are approximately 107 layers of CNC covering the droplets when 0.4% CNC is used.

None of the concentrations of CNC that have been used were found to be the critical concentration. But it can be assumed that since 0.1wt% CNC didn't help to form a stable emulsion, and then a certain value of CNC concentration more than 0.1% and less than 0.4% is the critical concentration.

2.3.4 Effect of ionic strength on the stability of the emulsions:

Ionic strength also has a significant effect on stabilizing emulsions. It plays an important role in the magnitude of electrostatic repulsive forces between droplets and CNC that take place when the system contains charged molecules. Electrostatic interactions play a very important role in determining the aggregation of droplets, and therefore emulsion stability is particularly sensitive to electrolyte concentration.

To examine how ionic strength affects the stability of the emulsions, a variety of different ionic strength NaCl solutions (zero, 0.305, 0.61, 0.95, and 1.9 M NaCl) were used to prepare different emulsions while keeping all other variables constant (CNC concentration equals to 0.8wt% and oil to water volume fraction is 5%). Interestingly, when using DI water with CNC the two phases tend to separate immediately after mixing, regardless CNC concentration or oil to water volume fraction that used. The same experiments as described before were carried out. As shown in Fig.9, using low ionic strength of NaCl, large droplets resulted when observed for

freshly prepared emulsions. After 24 hours of storage, droplets showed a significant increase in size, meaning that droplets grew rapidly with time. The high growth rate observations also occurred in the case of low CNC concentration to stabilize the emulsions. Contrarily, when higher ionic strength of NaCl was used, smaller droplets were formed and hence more stable emulsions were obtained. Also the growth rate was slower as evidenced by the droplet size not significantly increasing with time. Since high ionic strength screens repulsive electrostatic interactions between charged CNC; they are more likely to precipitate and adsorb onto the interface. (see Fig. 10 for droplets size distribution).

The data thus suggests an increased salt concentration promotes the coverage of CNC onto the oil-water interfaces and the subsequent formation of a strong network around the droplets. This network prevents droplet coalescence due to its rigid structure.

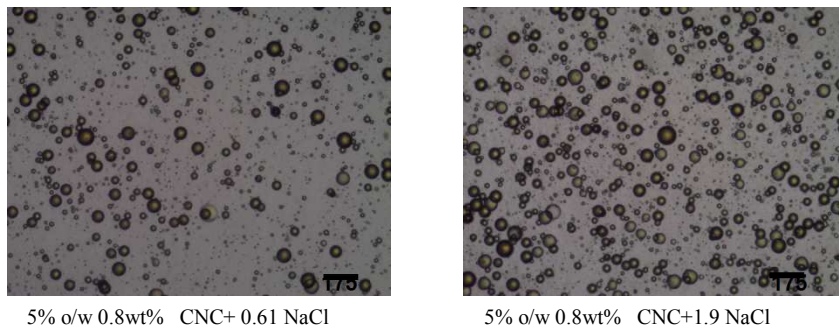


Fig.9: microscopic pictures of droplets for emulsions with different ionic strength, at zero time

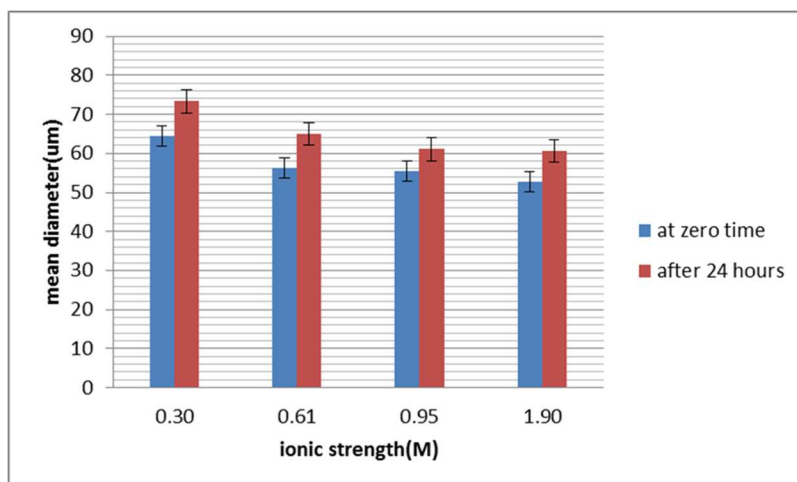


Fig.10: Droplets size distribution for emulsions with different ionic strength, at zero time and after 24 hours

In Fig.11, the effect of ionic strength of NaCl on the creaming rate of the emulsions is reported. Fig.5 illustrates that when ionic strength of NaCl increases, the rate of creaming is slightly increased; although the change is minimal. This result was not expected because as noticed in the previous section, smaller droplets and slower coalescence rates often correlated with slower creaming rates. Since the droplet diameter decreased with increasing ionic strength, this means that the creaming rate would be expected to increase as the salt concentration gets larger. However, emulsions that contain higher ionic strength of NaCl have a larger concentration of ions heavier than water. Most of those ions remain in the bulk solution around droplets. Consequently, the higher ionic strength aqueous phases have higher density which tends to increase creaming rates. In addition, a larger ionic strength is expected to result in more CNC aggregation which can have two different effects on viscosity.

If the aggregates remain dispersed in the aqueous phase, the viscosity would increase thus slowing down the creaming process. However it is more likely that the CNC aggregates would come out of solution and adsorb onto the interface, lowering the viscosity of the continuous phase and thus increasing creaming rates [32], [16]. In fact, because smaller droplets are formed at higher ionic strengths, it is expected that more CNC is adsorbed at the interface, consistent with a lower concentration of CNC in the aqueous phase. So even though higher ionic strength will promote stable droplets and relatively slow rate of growth, it causes slightly higher creaming rates and lead to faster phase separation.

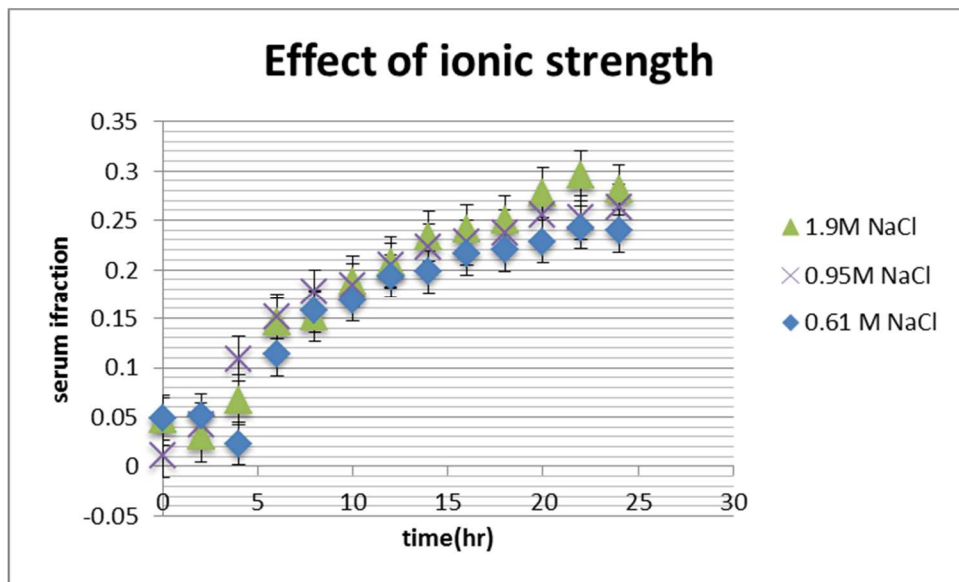


Fig.11: serum fraction vs time for emulsions prepared with different ionic strength

Results for creaming analysis and droplets size and size distribution show how increasing ionic strength helped increasing the stability by decreasing the droplets mean diameter and decreasing the rate of creaming. Also emulsions prepared by using CNC with DI water didn't help to form stable emulsions and the two phases separate immediately after mixing.

2.3.5 Effect of the presence of divalent ions on the stability of emulsions:

API brine consist of 2% CaCl_2 and 8% NaCl , and SSW contains 24.5% NaCl , 5.2% MgCl_2 and 1.6% CaCl_2 . To compare the monovalent with divalent ions in aqueous phases stabilized emulsions, emulsions prepared using API brine and 0.8 wt.% CNC were compared with those which is prepared using NaCl solution with 1.9M ionic strength(which is the API brine ionic strength).

The same for SSW, emulsions prepared using SSW and 0.8 wt.% CNC were compared with those which is prepared using NaCl solution with 0.6M ionic strength(which is the SSW ionic strength). Creaming analysis, droplet size and size distribution experiments were performed to analyze stability change with time.

Referring to Fig.12, it is clear that emulsions prepared using SSW showed less stability compared to 0.61 NaCl because of having larger droplets. And Fig.13 shows the size distribution of droplets and indicates that emulsions prepared using SSW have more large droplets and faster growing in droplet size. The same for emulsions prepared using API brine, results showed a little larger droplets than using 1.9 M NaCl .

The reason could be because of the presence of Ca^{2+} and Mg^{2+} divalent ions which might counter repel by having more affinity to opposite charged $-\text{OSO}-$ groups on the surface of CNC. Another hypothesis could be that high concentrations of electrolyte alter the structural organization of water molecules, which alters the strength of the hydrophobic interactions between non-polar groups. [32].

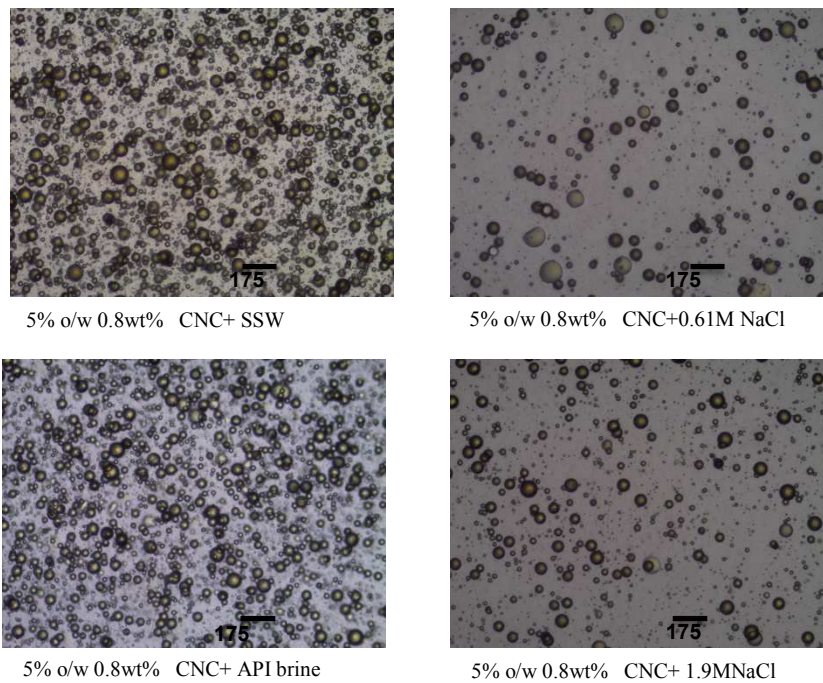


Fig.12: Microscopic pictures of droplets for emulsions prepared from SSW AND API brine v those prepared from only NaCl with similar ionic strength (0.61 and 1.9 M NaCl)

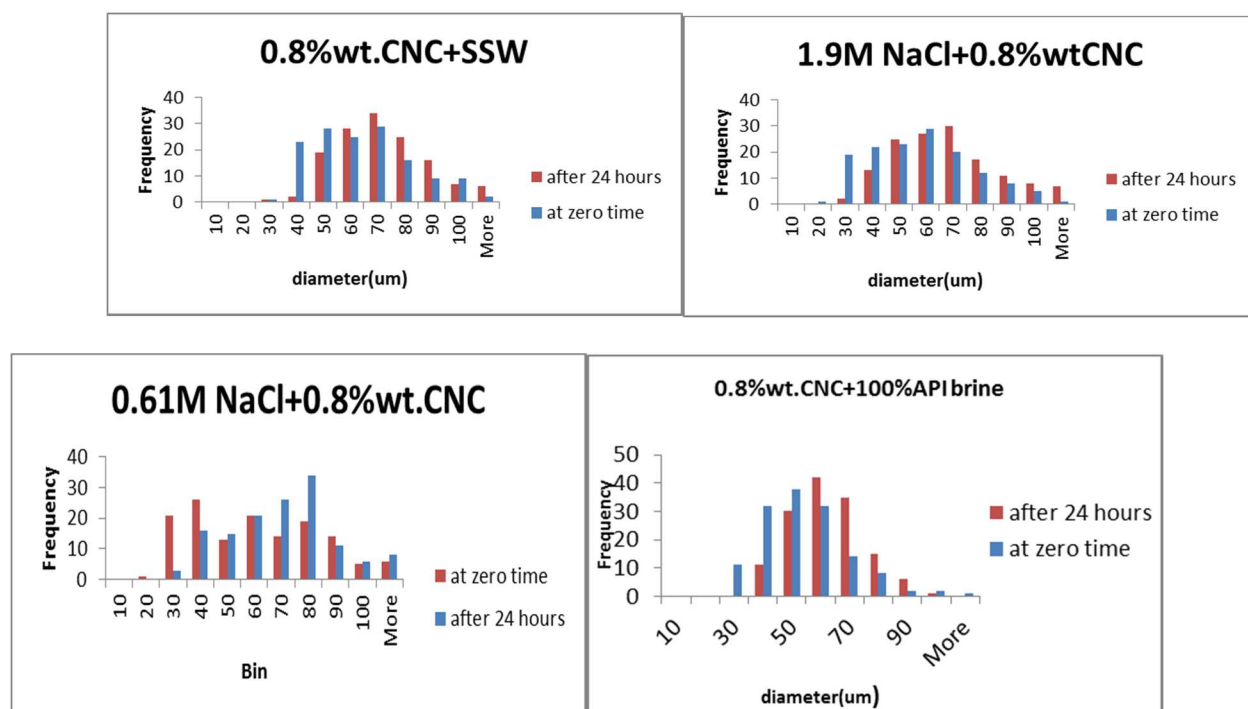


Fig.13: Microscopic pictures of droplets for emulsions prepared from SSW AND API brine v those prepared from only NaCl with similar ionic strength (0.61 and 1.9 M NaCl)

Fig.14 show the difference in creaming rates as a result of the difference of droplet size and size distribution and how fast the droplets grow. It implies that the presence of divalent ions Ca^{2+} and Mg^{2+} in the solution lead to an increased creaming rate compared with the only NaCl for preparing emulsions. This could be due to increased viscosity because of forming a network around CNC when ions bind to OH groups on its surface. [32]

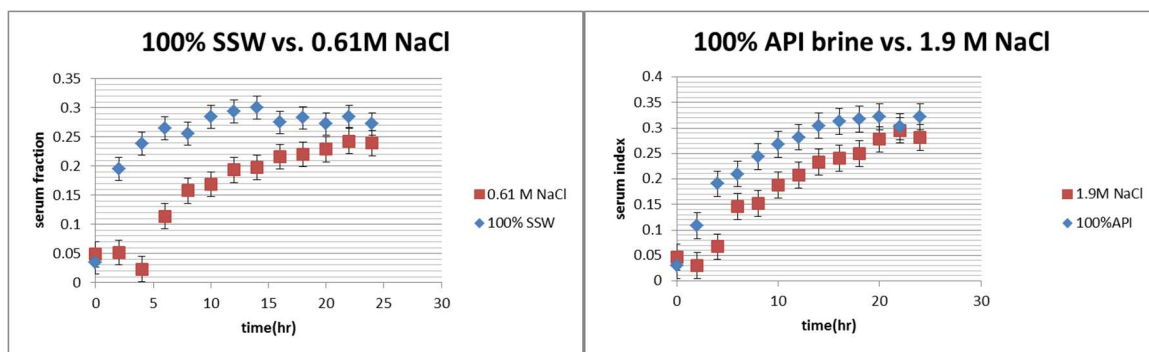


Fig.14: Creaming rates of emulsions prepared from SSW AND API brine v those prepared from only NaCl with similar ionic strength (0.61 and 1.9 M NaCl).

2.4 Conclusions

The study illustrated the efficiency of CNC as a stabilizing agent for crude o/w emulsions. It also showed that the stability of crude o/w emulsions was strongly affected by the concentration of CNC. As CNC concentration increases, the droplets were smaller in size and had a slower rate of growth therefore the stability of emulsion to coalescence increases. Though the use of CNC with DI water did not form stable emulsions, when combined with salt solution, efficient stability resulted. The stability of emulsions increases by increasing the ionic strength. CNC dispersions in salt solution increase the viscosity of the continuous aqueous phase. Thus any residual CNC aggregates that do not adsorb on the interface would improve stability by increasing viscosity. However, in the case of low CNC concentration (0.4 wt.%) this would be less likely to occur, consistent with the lower stability noticed.

2.5 Future work

The formation of stable crude o/w emulsions have been the focus of the past two years. Experiments that have been done illustrated some factors that affect the stability of emulsions such as CNC concentration, ionic strength of aqueous phase, and the presence of divalent ions. Future work concerns deeper analysis of emulsions destabilizing mechanisms in order to examine how to separate oil and water and extract oil from emulsions after the process of emulsification take a place. The influence of temperature on the stability of emulsions could be very interesting topic to focus on since temperature affects viscosity, density, mobility, and settling rate of solutions, it will have a significant effect on the stability of emulsions. Also since the previous study showed that increased ionic strength will increase the stability of the emulsions, desalination or dilution processes will be of interest in order to reduce the stability of the emulsions and extract oil. Other factors such as adding chemical demulsifiers and applying electrostatic fields that promote coalescence will be considered.

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VITA

OMAYMA Y ALAZZAM

Department of chemical engineering

University of Mississippi

Oxford, Ms, 38655

Omaimalazzam222@gmail.com

Personal Information:

Born: 04/22/1991, Jordan.

Citizenship: Jordanian

Education:

B.S., chemical engineering, 2015, Jordan University of science and technology, Irbid,
Jordan.

Professional Experience:

Training at ELI labs at Oxford Ms. Learning separation simple techniques and chromatography techniques. Also working on HPLI liquid chromatography and doing computer data analysis.

Research Interests:

I'm interested on studying and working on environmental chemistry topics and everything related to water and water pollution including cleaning up techniques . also interested on applying new technologies such as nanomaterials with great features on solving environmental problems .