DEVELOPING BIOCOMPATIBLE WIDE TEMPERATURE-RANGE FUNCTIONAL

HERDERS FOR RAPID OIL SPILL RESPONSE

A Thesis

by

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ABSTRACT

The effect of oil spills in marine environment has resulted in huge negative environmental impacts and economic loss. The Deepwater Horizon oil spill of 2010 is the most recent, and the worst spill in the world, which affected more than 8000 kinds of marine organisms and cost around $65 Billion. Hence, it is imperative to have in place an effective and efficient oil spill recovery system.

The research focuses on developing a chemical oil recovery method called oil herding. Herder is an amphiphilic oil-collecting agent, that is designed to spray around the oil spill areas and can retract oil slick from a thin layer to a thick mass, which is easier for further spill recovery. The application of oil herder lowers the air-water tension and causes retraction of the oil slick.

The commercial oil herders like Silsurf A108 and Silsurf A004-D are effective, but their toxic impact to environment is undocumented, and they are chemically stable, which makes them remain on water body for a long period. The proposed project aims to develop an innovative oil herder from a natural plant-based product, Konjac. The base material used to develop the proposed oil herder konjac is derived from konjac root, commercially known as konjac glucomannan (KGM). KGM is a natural polysaccharide and has flexibility in functionalization. The easily functionalized hydroxyl groups in the KGM molecular structure allow hydrophobic tails to be attached to the hydrophilic backbone to form the surfactant-like structure. The functionalized KGM is demonstrated in this research to efficiently herd lighter oils like dodecane. KGM was found to have no

Krafft temperature and that enables it to be effective in herding oil in cold waters. The applications of KGM based surfactants as dispersants or as agents aiding dispersants in oil spill mitigation is an area which augurs more research.

DEDICATION

To Mom, Dad, Rini, and Sangeeta.

ACKNOWLEDGEMENTS

I would like to thank my committee chair, Dr. Cheng, and my committee members, Dr. Rogers and Dr. Banerjee, for their guidance and support throughout the course of this research.

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NOMENCLATURE

CMC   Critical Micelle Concentration

DMF   Dimethylformamide

DMKGM   Degraded Modified Konjac Glucomannan

ISB   In-situ burning

KGM   Konjac Glucomannan

MKGM   Modified Konjac Glucomannan

NCEBR   The National Center for Electron Beam Research

PEG   Polyethylene Glycol

SDS   Sodium Dodecyl Sulfate

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1. INTRODUCTION

1.1. Oil spill and its detrimental effects

The petroleum products play a pivotal role to help humans maintain a decent standard of living. Petroleum products in form of energy, fuel and other essential commodities like plastics and pharmaceuticals are inevitable from the modern society. There has been a steady increase in the requirement of the petroleum products, and this trend may stay for some time to come. The increase in demand of petroleum products has increased its exploration, production and transportation. (International Energy Agency, 2018). The oil from its exploration fields to the end user moves along different transportation modes, including tankers, pipelines, railcars, and tank trucks. Oil is stored and processed along these different modes at terminals and refineries. An oil spill can take place at any point in these transportation modes, storage or processing locations. (Fingas, 2010)

The effects of oil spills in marine environment have resulted in huge negative environmental impacts and economic losses. The spilled oil generally has the tendency to float on the water surface and spread along due to low specific gravity and low surface tension. The spilled oil has the capability to affect the delicately poised marine ecosystem and can trigger a domino effect, which can bring about impacts even to coastal belt and human lives. Hence, it is imperative to have in place an effective and efficient oil spill recovery response system. The major oil spills that occurred are; Gulf war (1991) oil spill, which discharged 240 million gallons; Deepwater Horizon (2010)

released approximately 132 million gallons of oil; Ixtoc 1 (1979) discharged 140 million gallons; Exxon Valdez (1989) spilled 11 million gallons of oil. Out of these BP's Deepwater Horizon alone cost $65 Billion. These large-scale oil spills have huge socio-economic impacts and often gain media and public attention, because of their long-term effects. However, there are many oil spills that are smaller in magnitude but more common in occurrence that accounts for 70% of the total spill cases so far. These small oil spills evade attention, and there are not many effective mitigation systems for these spills. Oil spills can be of varying magnitude and nature depending on the properties of the oil, it can be crude oil, heavy or light oil, or processed petroleum products. The spill occurring on land and on water have different environmental effects. Additionally, weather and geographic location of the place also determine the effect of the spill. (Fingas, 2010)

The oil spills on water bodies pose different challenges, and the oil spill recovery system for this is the focus area of this research work. Oil spills leave both short-term and long-term effects on the aquatic ecosystem. An account of environmental damage due to BPs Deepwater Horizon oil spill depicts the detrimental effect of a large-scale oil spill. The depletion of fish population, the effect on the sea birds, and other animals depended on coastal belt ecosystem, the health and well-being of human population along the coastal belt affected are studied in detail by various agencies. It is estimated that over 20 million hectors of the Gulf of Mexico were closed for fishing, and it had huge economic effect on the fishing communities. The impact assessment of oil spill is

still on-going to evaluate the long-term effects. (Barron, 2012) (Impact Assessment, Inc., 2001)

1.2. Oil spill recovery system

The most preliminary method of containment and recovery is the mechanical method using booms, barriers, and sorbents, as shown in Figure 1-1(a). They can be ineffective and resource intensive due to external conditions such as water currents and wind turbulence. Adopting chemical and biological methods as a combination with mechanical method is effective in reducing the spread of oil spills to the coastal and other less accessible areas. The commonly used methods are dispersing agents, biological agents and gelling agents. The dispersing agents are surfactant that help break the oil into smaller particles and hence make them disappear from the water surface, as shown in Figure 1-1(b). Biological agents involve microorganism which can eat up or degrade the oil spill and make them less harmful. The gelling agents are effective where the water current is high, and the oil is mixed to form gel like substance which can then be mechanically recovered from the water surface. (Agency, 1993)

Another effective chemical method to deal with oil spills is the herding method. The herders help reduce the air-water interface surface tension and helps the spilled oil to herd and form a thick slick, preferably 3mm thick layer which will then favor in-situ burning (ISB). This combination of oil herding and in-situ burning method is particularly effective in remote, ice-covered waters where mechanical methods and other chemical methods are practically difficult to implement. (S.L. Ross Environmental Research Ltd., 2012)
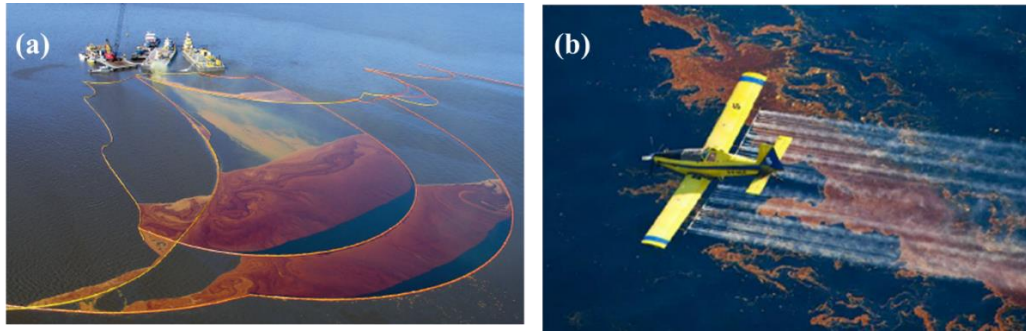
Figure 1-1: The various methods of oil spill recovery (a) Mechanical recovery using booms (b) Releasing dispersants from aircrafts (NOAA Office of Response and Resotoration) (Gulf of Mexico Research Initiative (GoMRI), 2010-2017)(Courtesy GoMRI)

1.2.1. Chemical herding and its effectiveness in remote ice-covered waters

A series of oil herding experiments conducted by SL Ross Environmental Research Limited initiated in 2004 and continued till 2014 proved that oil-herding is the most effective oil spill response technique that can effectively replace mechanical booms to thicken the oil spill in remote, ice-covered waters. The experiments were carried out using the herding agents ThickSlick 6535 and OP-40 which were defined by U.S. EPA as "Practically non-toxic". These chemical herders are hydrocarbon based and they are applied by dissolving in a hydrophobic solvent 2-ethyl 1-butanol which however has toxic effects. The method of ISB after herding the oil is found to be effective for Arctic spills, as the low water temperature was found not to have any detrimental effect on the burn rate of the fire. (S.L. Ross Environmental Research Ltd., 2012). The small-scale testing in 10 m^2 pan showed that the oil herded increased the spilled oil thickness to 3 mm in 30 minutes and to around 5 mm in 60 minutes. It is experimentally evident that the oil herding is successful in low temperature ice-drift waters which is 2°C. One

notable drawback of using chemical herders at the freezing temperatures was the gelling and increased viscosity of the herder, causing difficulties in dispersing the herder from the discharge nozzle. This issue was solved by increasing the concentration of solvent, which brought down the gelling point to -17°C.

SL Ross team also experimentally demonstrated that herders improve other marine spill response operations like skimming and oil dispersing in arctic conditions. The skimmers tend to collect ice pieces along with oil, rendering it ineffective, whereas application of herders can collect the oil into thick slick without moving the ice. These concentrated oil layer can then be effectively removed using the skimmers and mechanical booms.

The oil dispersants action when applied on the oil layer, depends on the thickness of the oil layer. Where the oil layer is too thin, the dispersants immediately drop to the underlying water without effectively able to capture oil. When the dispersant falls directly on the water it acts as herders and thickens the oil layer which acts against the work of dispersants, resulting in wastage of those dispersants. In such cases, the herders can be applied along the edge of the oil layer and thickening the oil to a suitable range and then applying the dispersants on the retracted oil layer which has a smaller surface area. This synergy of herders with other oil recovery mechanisms is effective in Artic waters. The large-scale experiment of oil spill conducted by SL Ross team is shown in Figure 1-2.
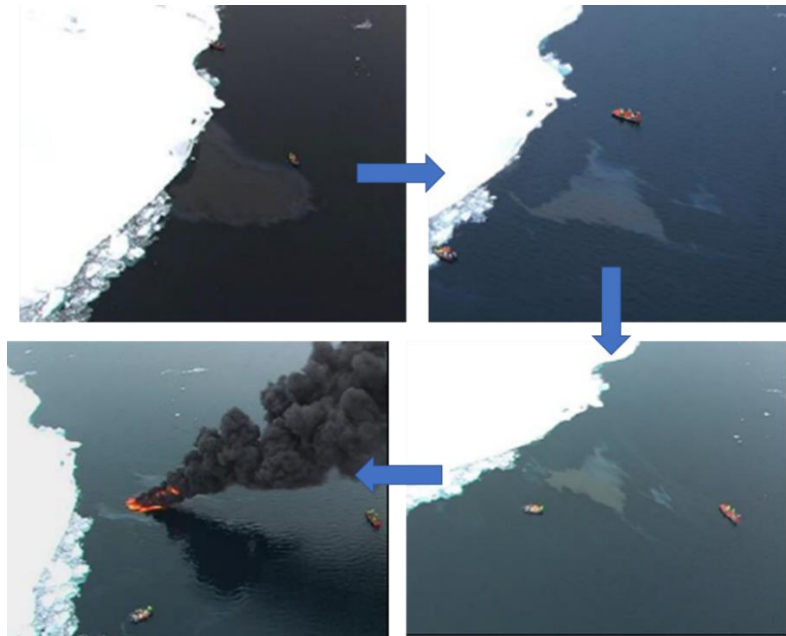
Figure 1-2 The experiment done by SL Ross Team showing the combination of oil herding and in-situ burning in Arctic waters (S.L. Ross Environmental Research Ltd., 2012)

1.3. The theory of oil herding

When oil is spilled on the water surface, the oil tends to spread out and stabilize attaining a very thin layer. Initial spreading of oil is due to the gravitational force. When the oil layer becomes very thin, then the spreading takes place due to the net spreading force. (Fay, 1969). The net spreading force is the net surface tension of the oil, air and surrounding water.

The water is highly polar and has high surface tension (70 ~ 75 mN/m). The water molecules have cohesive forces that act among them. In the bulk phase, water molecules experience attractive forces to all the other molecules around them thus cancelling out the forces in opposite directions. Whereas, a water molecule on the air-water interface experiences imbalance in this attractive force, since the forces between

the air and water molecules are insignificant when compared to the forces between water

molecules, resulting in a net force towards the water bulk phase. This net inward force

causes the outer water molecules to occupy the least surface area and act as a stretched

membrane giving it a high surface tension or water-air ($\gamma_{A/W}$) surface tension. The oil on

the water layer experiences two kinds of interfacial tension, the oil-water ($\gamma_{O/W}$) and the

oil-air ($\gamma_{O/A}$) in the opposite direction as ($\gamma_{A/W}$), as shown in Figure 1-3 (a). The value of

$\gamma_{O/W}$ and $\gamma_{O/A}$ depends on the chemical properties of the oil and the water, however, an

approximate value of the sum of $\gamma_{O/W}$ and $\gamma_{O/A}$ for a typical crude oil is 25 mN/m. This

imbalance in surface tension causes the oil to spread once spilled on the water surface.

The application of oil herder lowers the air-water tension ($\gamma_{A/W}$) to values below 25 mN/m

and causes retraction of the oil slick, as shown in Figure 1-3(b). (Deeksha Gupta, 2015).

The herder structure consists of a hydrophobic tail and a hydrophilic head. The

hydrophilic head dissolves on the water surface and forms the monolayer, and the

hydrophobic tail forms an interface between the air and the water, which in effect

reduces the air-water surface tension.
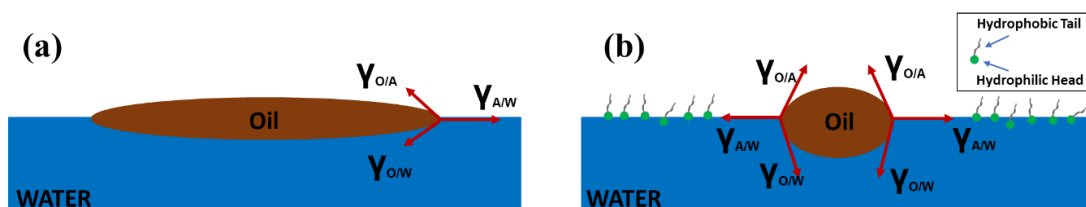
Figure 1-3: Schematic of theory behind oil herding

The main advantage of oil herding technique is that it does not require a "wall" to push against to retract the oil layer. Thus, this method is applicable in open sea waters.

1.4. Konjac as base material to synthesize oil herders

This study focuses on using the Konjac - a natural polysaccharide that is mostly grown in Asian countries like China, Japan, and Thailand, as shown in Figure 1-4. The current use of konjac in the west are in the food and nutraceutical industries. The purified konjac flour known as Konjac Glucomannan (KGM) is now extensively used in food production and food additives. Natural polysaccharides are gaining interest in the field of polymeric surfactants as they are easily available, environment friendly, and non-toxic. (Fanbing Meng a, 2013)

Figure 1-4: Konjac corn and konjac inflorescence (http://www.konjacfoods.com/noodles/index.htm, n.d.)

Konjac being a polymeric surfactant has added advantages in flexibility functionalization. The easily functionalizable hydroxyl groups allows the introduction of

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hydrophobic tails to the hydrophilic backbone of the surfactant structure. This allows altering its surfactant properties to bring about applications in various fields, especially in oil herding. (Patrizio Raffa, 2015)

KGM is composed of 1,4-linked D-glucose and D-mannose residues as the main chain, with branches through β-1,6-glucosyl units. The degree of branching is estimated at approximately 3 for every 32 sugar units. It consists of mannose and glucose units in a molar ratio of 1.6:1, and the acetyl groups along the KGM backbone, which contribute to solubility properties are located every 9 to 19 sugar units at the C-6. The Chemical structure of KGM is shown in Figure 1-5. (Melinda Chuaa, 2010). The details of hydrophobic modification carried out in KGM is described in section 2.2.
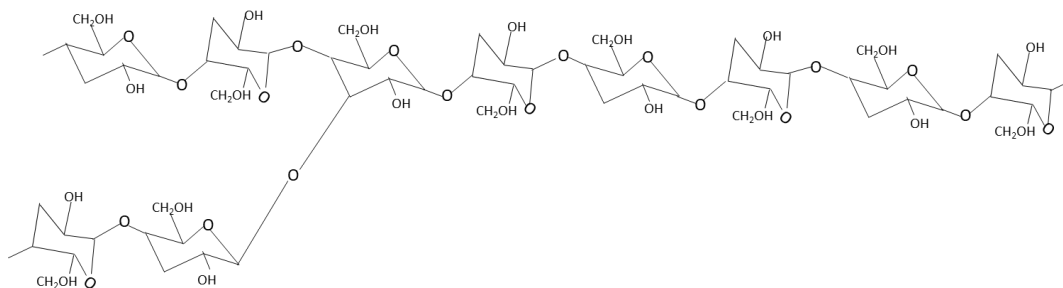
Figure 1-5*:* Chemical structure of KGM (Melinda Chuaa, 2010)

1.5. Research objectives of the thesis

Objective 1: To hydrophobically modify KGM and to investigate its oil herding properties. Will carry out various chemical synthesis to attach hydrophobic tails to the

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KGM structure and identify the process that gives the best results with respect to the specific surfactant properties like emulsification and oil herding.

Objective 2: To examine the oil herding capability of modified KGM in low temperature waters. Will compare the efficiency of oil herding with modified KGMs in normal temperature water to that in low temperature waters and identify the effect of low temperature water in oil herding.

Objective 3: Identify possible applications on modified KGMs in the oil spill recovery process. Will examine the applicability of modified KGMs as dispersants, which is a typical oil spill mitigation method being adopted worldwide.

2. HYDROPHOBIC MODIFICATION OF KGM AND INVESTIGATING ITSEMULSIFYING AND HERDING PROPERTIES

2.1. Summary

KGM being a natural polysaccharide makes it easily modifiable and the hydroxyl groups act as the target group for the reactions to take place. The polymer chain of the KGM has hydroxyl groups, which makes it highly soluble in water and this polymer chain acts as the hydrophilic head of the polymeric surfactant. The process of attaching the hydrophobic tail to the polymer chain is called the hydrophobization reaction. In this research the hydrophobization of konjac using octadecyl isocyanate in ethyl acetate solution is adopted. Further, the product is reacted with the 1,3-Propane Sultone and potassium carbonate in the solvent Dimethylformamide (DMF) to add charges to the structure to reduce the coagulation of the grafted hydrophobic tails. The modified KGM (DKGM) acquired a surfactant like structure. The surfactant's emulsification property and its potential to herd oil is demonstrated on a lab scale set-up. The preliminary results with estimation of the conditional time ranges to herd the oil will be the basis to judge the effectiveness of the KGM based surfactant

2.2. Materials and Methods

2.2.1. Materials used for the synthesis of the herder

The following materials were used to functionalize the KGM surfactant: Konjac powder Ticagel® Konjac High Viscosity TIC GUMS, which is used as the base material

to synthesize the surfactant, octadecyl isocyanate, ethyl acetate, 1,3 Propane Sultone, potassium carbonate and NN- dimethyl formamide.

2.2.2. Synthesis of the herder

The synthesis of the herder is carried out in a two-step process, as shown in the figure 2.1. The first step is the hydrophobization of the KGM. The sequential procedure for step is, the base material Konjac powder Ticagel® (KGM) is first dried in a vacuum drier for 24 hours to remove residual moisture present in the powder. The vacuum dryer is used instead of a laboratory equipment dryer, because the warm air circulating inside the dryer can alter the properties of the KGM. KGM (5 g) is taken in a 250 ml round bottom flask and ethyl acetate (100 ml), and the solvent for the reaction is added to it. The mixture is shaken manually for 1 minute and then sonicated in for 15 minutes in VWR Model 50T Ultrasonic cleaner to get a homogenous mixture. The hydrophobization of KGM is carried out using octadecyl isocyanate, the hydrophobic tail that is grafted to the KGM structure. Octadecyl isocyanate (1 g) is added to the round bottom flask and then sonication is repeated for 15 minutes. The chemical grafting takes place under continuous stirring for 4 hours at 60ºC. The reaction mixture is centrifuged in Thermo Scientific CL 2 Centrifuge at 3000 rpm for 2 minutes to separate the solvent from the reacted mixture. The residue mixture is again washed in ethyl acetate and re-centrifuged at 3000 rpm for 2 minutes. The excess ethyl acetate is drained out and the residual mixture is dried in the Welch Model 2027 Self- Cleaning Dry Vacuum System for 2 hrs. The step 2 comprises of attaching charges to the polymeric chain. The steps followed are, the residual sample (1 g) from step one is taken in a 250 ml round bottom

flask. 1,3 Propane Sultone (0.5 ml), potassium carbonate (0.15 g) and the solvent NN-dimethyl formamide (20 ml) is added to the sample, and the mixture is continuously stirred for 2 hours at 65°C. The reaction mixture is centrifuged in Thermo Scientific CL 2 Centrifuge at 3000 rpm for 2 minutes to separate the solvent from the reacted mixture. The residue mixture is again washed in acetone and re-centrifuged at 3000 rpm for 2 minutes. The acetone is drained out, and the residual mixture is dried in the Welch Model 2027 Self- Cleaning Dry Vacuum System for 4 hours.

Octadecyl Isocyanate

1,3 Propane Sultone
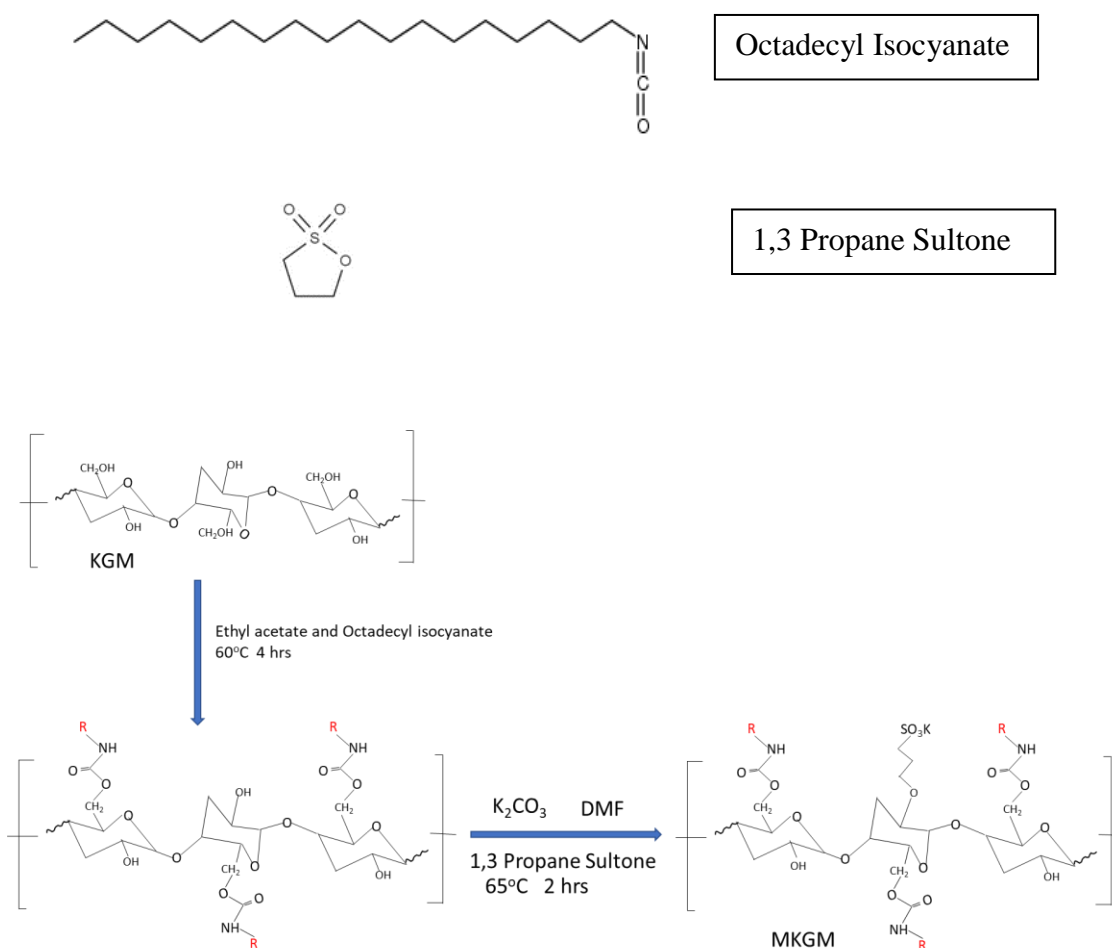
Figure 2-1: Hydrophobic modification reaction on KGM

2.2.3. Characterization using FTIR

The characterization of pure KGM and the MKGM was carried out using FTIR. The peaks at 1400 cm^{-1} and at 1600 cm^{-1} are the attachment of S=O and C=O groups in the MKGM structure showing the hydrophobic modification reaction has taken place.
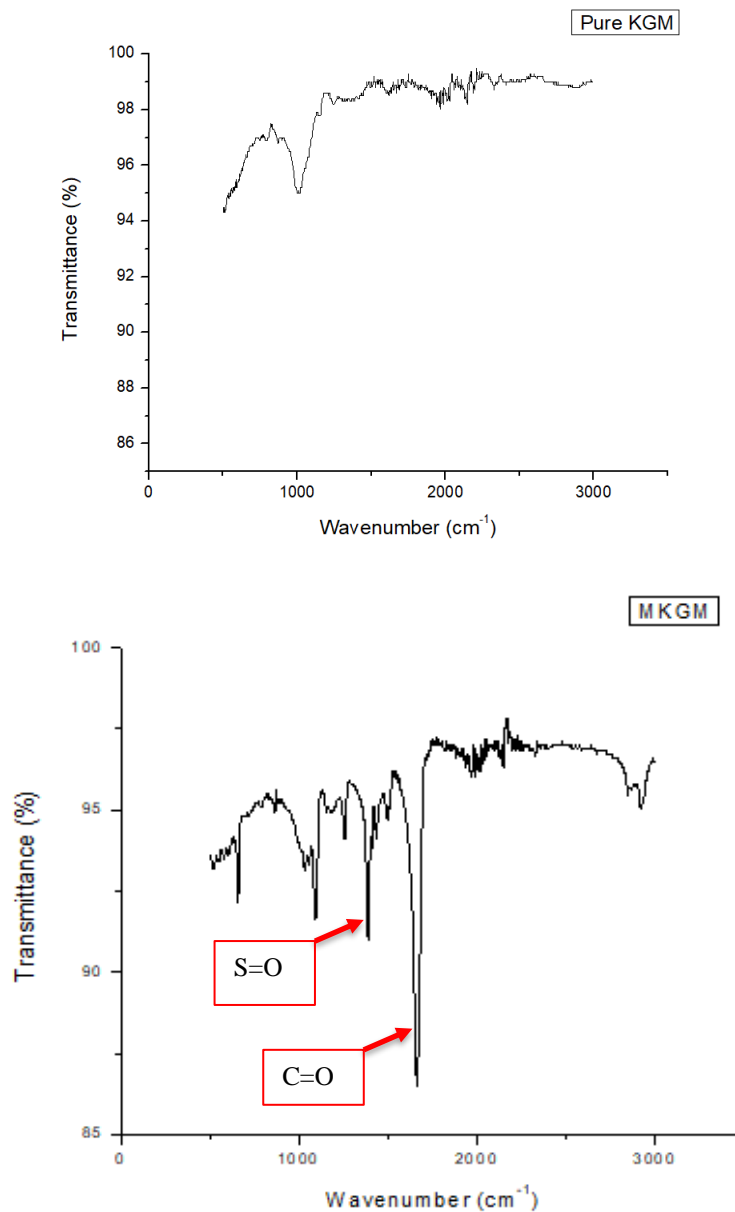
Figure 2-2: FT-IR spectra of pure KGM and MKGM

2.3. Emulsification property of modified KGM

The hydrophobic modification of KGM gives it a surfactant-like structure and alters its interfacial properties. To observe the changes in the interfacial properties of the modified KGM (MKGM), 4 ml MKGM solution in water in ratio 0.0025 (wt/vol) was mixed with 4 ml of red pigmented dodecane in a vial. The red pigmentation to the dodecane was provided by adding Sudan IV powder. Similarly, 4 ml of pure KGM solution in water in ratio 0.0025 (wt/vol) was mixed with 4 ml of red pigmented dodecane in a vial. Both the mixtures in the vial were shaken manually for 30 seconds and were left undisturbed for 48 hours. Figure 2.3 shows photograph of both the vials taken at the start of the experiment and after 48 hours.
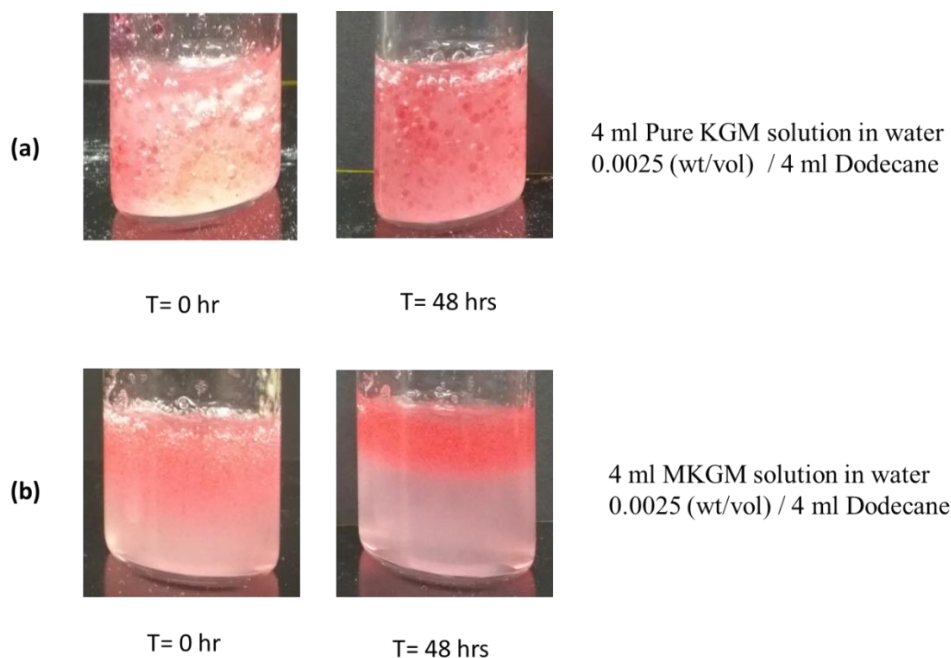
Figure 2-3: (a) Photographic images showing the dodecane and pure KGM forms a gel-like mixture (b) Images showing the emulsion formed by MKGM and dodecane
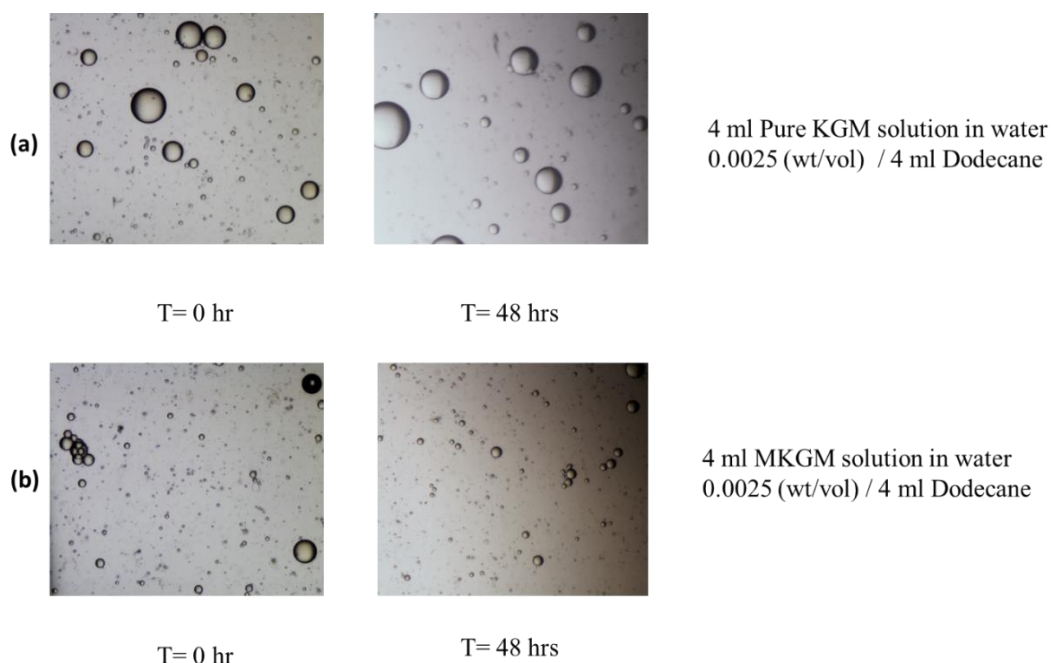
Figure 2-4: (a) Optical microscopic images showing the pure KGM form a gel-like mixture (b) Optical microscopic images showing the emulsion formed by MKGM

KGM is a long chain polymer (polysaccharide) known for its ability to form gels when dissolved in water. The presence of large number of hydroxyl (-OH) groups helps it bind the water molecules resulting in a viscous mixture. The gel like property is attributed to the cross-linked network formed within the water. (Dipjyoti Saha, 2010) (M. Davidovich-Pinhas, 2014). Figure2.3(a) shows the gel like mixture of dodecane in water due to the cross-links provided by KGM and shows high stability of the gel-like mixture when observed after the 48th hour. Figure 2.3(b) shows the oil-water emulsion formed with the help of MKGM and the stability of the emulsion after 48 hours. The optical microscopic image of the pure KGM in oil-water mixture shown in figure 2.4(a) clearly show the oil droplets trapped in between the water bound by the cross-links of

the pure KGM. Figure 2.4(b) show the optical microscopic image of the oil-water

emulsion at the start and at the 48th hour. The relatively smaller oil droplets when

compared between figure 2.4(a) and 2.4(b) is indication of the surfactant nature of

MKGM. The relatively similar size of the oil droplets at t = 0 hour and at t= 48 hour

shown in figure 2.4(b) is due to the resistance to coalescence of oil droplets resulting in a

highly stable oil-water emulsion. The MKGM engulfs the oil droplet and forms a layer

around it, as shown in figure 2.5(b) with the hydrophobic tail anchoring to the oil droplet

and the hydrophilic head outwards in contact with the water.
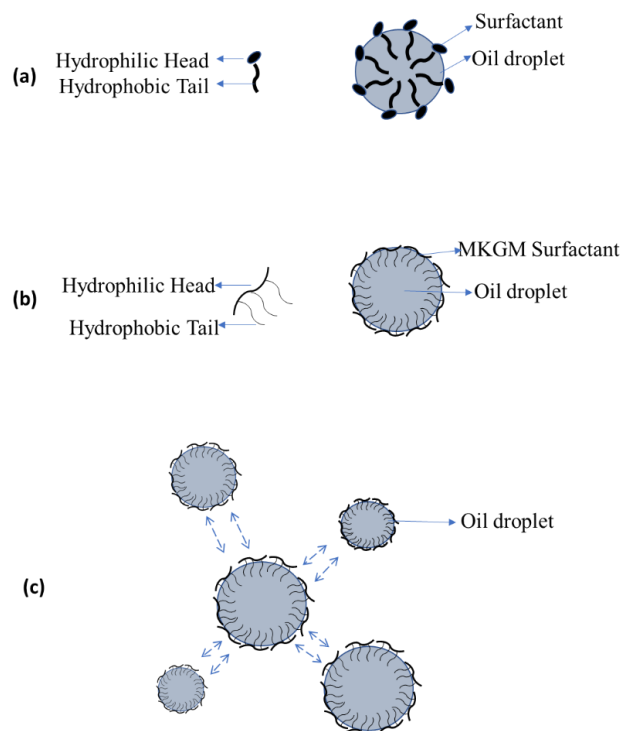
Figure 2-5 (a) Schematic of a typical structure of a surfactant and surfactant aiding an oil-water emulsion (b) Schematic of a MKGM surfactant when engulfing an oil droplet (c) Schematic showing the stabilization of oil droplets in the water due to combination of steric and electrostatic repulsion.

The stability of the oil-water emulsion induced by adding the MKGM is expected due to the combination of steric and electrostatic repulsion between the surfactant engulfed oil droplets, as shown in figure 2.5(c) (Pradeep Venkataraman, 2013)

This emulsification property of MKGM can be exploited in the treatment of oil spills with dispersants. Dispersants are surfactants used on the spilled oil to aid the breaking of oil into small droplets due to the reduction in interfacial-tension. The conversion of oil layer formed on the water surface to small oil droplets enhances the bioremediation of the oil spills. As proven by Pradeep Venkataraman et. al, the hydrophobically modified chitosan -a biopolymer can be used to considerably enhance the stability of crude oil droplets, which are dispersed by the chemical dispersant Corexit 9500A and help in reducing the use of Corexit 9500A.

2.4. Oil herding using MKGM

MKGM is showing surfactant properties as discussed in the previous section. The next step is to observe whether MKGM shows any interfacial property that helps it to form a monolayer on the water surface owing to its amphiphilic surfactant nature. The science of oil-herding is explained in chapter-1 and the same principals are used to observe if MKGM shows any oil-herding property.

2.4.1. Oil herding experiment set-up and results

To simulate oil herding experiment on a lab scale, 22°C water is taken in a Pyrex® 190 X 100 dish. The diameter and height of the dish is 190 mm and 100 mm, respectively. Then 0.4 ml red pigmented dodecane is carefully applied on the water surface using a transfer pipette and waited until the oil has spread out and stabilized.

Once the oil layer is stable, 0.4 ml herder (MKGM/ water ratio 0.0025 (wt/vol) is

applied around the edges of the oil layer using a transfer pipette. The schematic of the

experiment setup is show in figure 2.6.
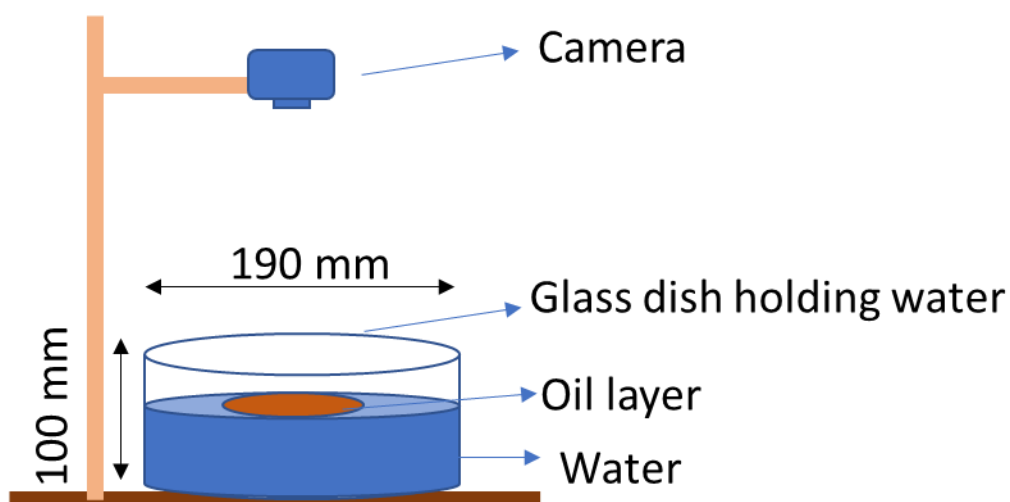
Figure 2-6: Schematic of the oil herding testing setup

The oil starts to retract slowly. The images of the herding process are taken at

regular intervals and when the retracted oil attains stability. The approximate time when

the oil retraction becomes stable is noted as the total herding time, which was observed

to be 45 minutes. Using the image processing program ImageJ, the surface area of the

oil layer and the retracted oil is calculated, as shown in figure 2.7(a) and 2.7(b). Based

on the volume of the oil added the thickness of the herded oil is calculated. The area of

the oil retracted from 101.5 cm^2 to 19.65 cm^2, that is an area reduction of 80.61 % in area

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and the oil thickness increased from 0.039 mm to 0.2 mm, that is an increase of 413 % in thickness.

(a

Area of the oil layer = 101.50 cm^2

Thickness of the spread oil layer = 0.039 mm

T= 0 min

(b
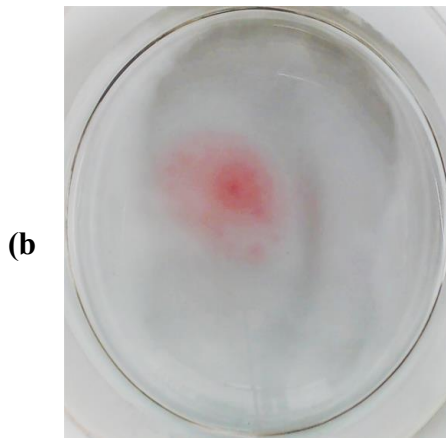
Area of the oil layer = 19.65 cm^2

Thickness of the herded oil layer = 0.2 mm

T= 45

Figure 2-7: The oil spill and herding simulated on lab-scale setup

The oil herding process is observed to be extremely slow with total time of 45 minutes. This demonstrates that MKGM surfactant has herding property and reduces the air-water surface tension that causes the oil layer to retract. The efficiency of the herder is attributed to the time taken for the herder to herd the oil. In this case, MKGM has

extremely low efficiency. This low efficiency might be attributed to the hydrophilic

polymer backbone of the KGM, which makes it hard to form a monolayer on the water

surface. The same oil herding was tested using the Texas Crude oil and the MKGM

herder did not show capability to herd the crude oil. This may be because the high

viscosity and very low oil-air surface tension of the crude oil, which require larger

reduction in the air-water surface tension by application of the surfactant to cause the

crude oil to retract. This shows that the reduction in interfacial tension caused by

MKGM surfactants are not very high indeed.

2.4.2. The MKGM surfactant behavior after diffusion in water

The bulky and long hydrophobic chain increase the time take to form the

monolayer on the water surface, as shown in figure 2.8.
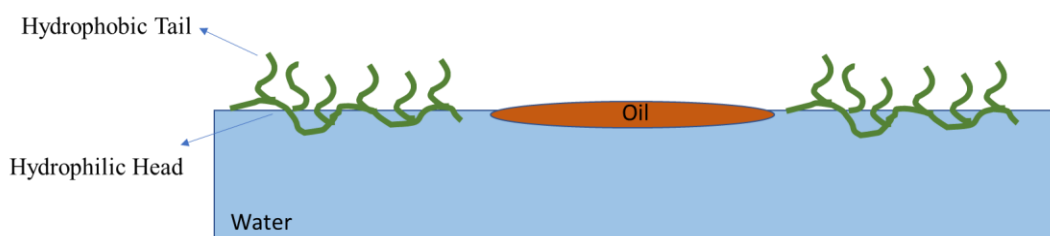
Figure 2-8: Schematic of the MKGM surfactant forming monolayer on the water surface.

This lag time for the MKGM surfactant to adsorb to the air-water interface to

form a monolayer may be attributed to many factors. The macromolecules of MKGM

that is in the solution needs to diffuse to the surface so that the hydrophobic tail reduces

its interaction with the water molecules and stays in contact with the air, as shown in figure 2.9 (a). After reaching the surface, the surfactant macromolecules will tend to stretch-out and form a straight chain along the surface with the hydrophobic tail attaching itself to the non-polar phase. The nature of the hydrophobic tail and its affinity to non-polar phase can determine the time taken for the tails to anchor to the non-polar phase, as shown in figure 2.9(b). The stiffness of the hydrophilic backbone also determines the rate at which the stretch-out takes place. (Desbrièresb, 2004) (Widad Henni, 2004)
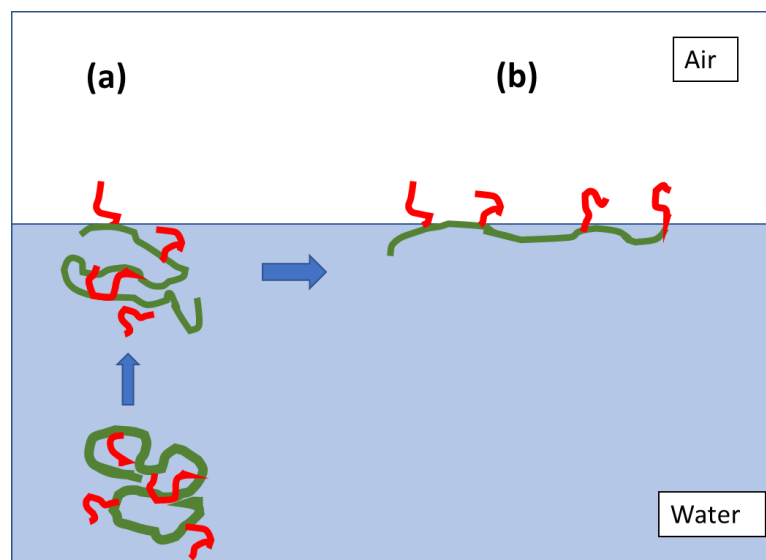
Figure 2-9: The macromolecules of MKGM diffuse to water surface and forming monolayer

The slowness of the herding may also be attributed to the inability of the MKGM surfactant to reduce the air-water surface tension to the desired level. This may be due to geometry and physical packing of the hydrophobic tails along the interface. The

schematic arrangement of hydrophobic tails along the water surface in dense packing

and in less dense packing is shown in figure 2.10(a) and 2.10(b). The surface tension

reduction is higher when the hydrophobic tails arrange densely as in figure 2.10 (a) as it

forms a near perfect layer between the water and the air, reducing the interaction of

molecules of both phases.
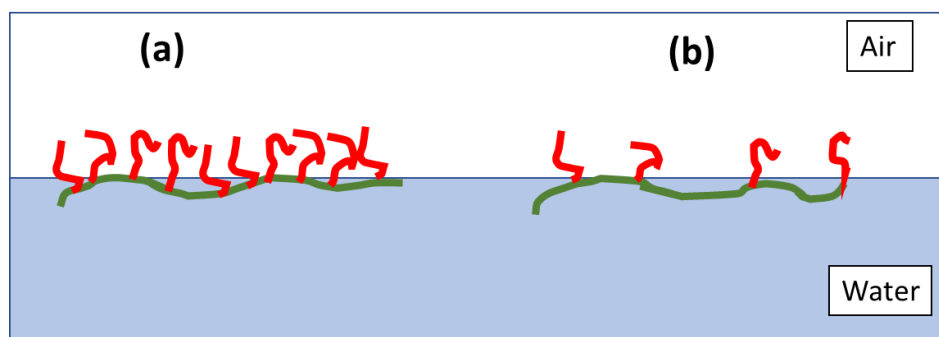
Figure 2-10: The schematic of arrangement of hydrophobic tails along the water surface in (a) dense packing and in (b) less dense packing

The hydrophobic tails may also show attraction towards each other that would

account for the formation of dense aggregates of hydrophobic tails causing the polymer

backbone to coil inwards and reduce the number of hydrophobic tails settling on the air-

water interface, as shown in figure 2.11(a). The MKGM surfactant structures bulk

dilution will result in interfacial polymer arrangement, as shown in figure 2.11(b). This

tendency of MKGM surfactants to coil inwards will increase its stabilization time at the

air-water interface. (Widad Henni, 2004)
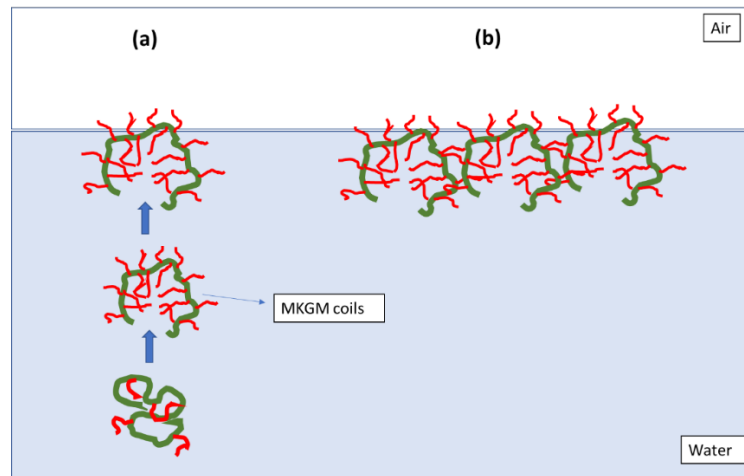
Figure 2-11: The schematic of bulk dilution of MKGM in water

2.5. Effectiveness of modified KGM as dispersants

Dispersants as a method for oil spill recovery is extensively used due to its effectiveness in high wave conditions and its low resource intensive method of application make it a quicker response option. The possibility of application of dispersants from aircrafts make it a preferred option if the spills occur at deep waters where it takes time for resources through ships to respond. Dispersants are surfactants that when falls on the spilled oil, wraps around the oil, form small droplets and forces these droplets to descend downwards to the bulk water phase and disperse and then allows itself to biodegradation by aquatic microbes. (United States Government Accountability Office, 2012)

2.5.1. Demonstration of using KGM as dispersant

A similar set up as described in section 2.4.1 is used here. 2 ml of Texas Crude is applied on the water surface, which is at 22°C. The top view and side view of the crude

oil is shown in figure 2.12 (a). 0.5 g of pure KGM powder is dispersed on the oil layer, and the observations are shown in figure 2.12 (b) showing the gelation of the KGM and the crude droplets. The MKGM powder is dispersed on the oil layer, and the dispersion of oil droplets was observed, as shown in figure 2.12 (c).

This experiment demonstrate that the MKGM can be used as dispersants.
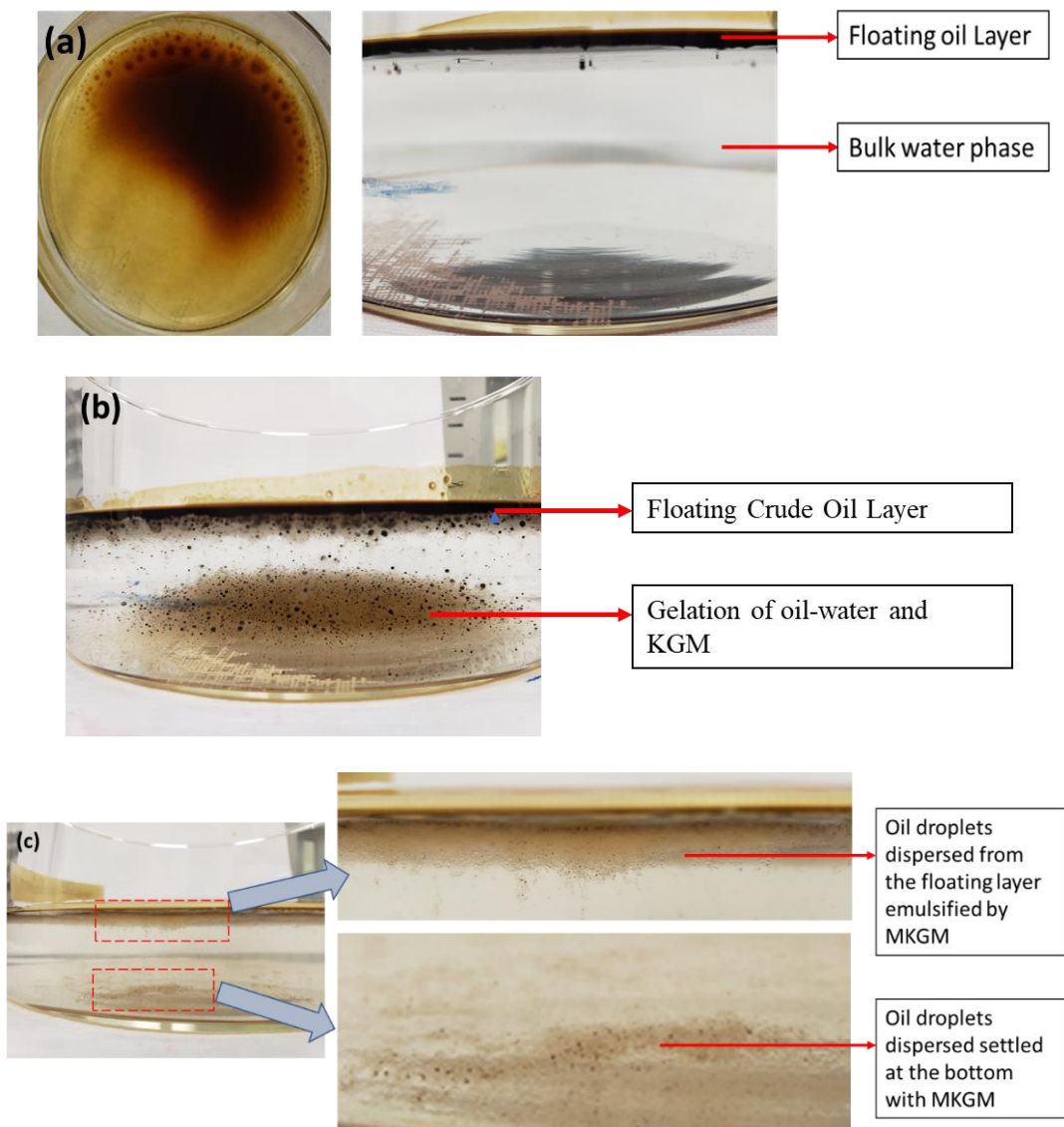
Figure 2-12: Demonstartion of MKGM used as oil dispersant

2.6. Conclusion

The hydrophobic modification of KGM has introduced surfactant property to it, and the functionalization is characterized using FT-IR. The long polymeric chain of KGM acts as the hydrophilic backbone, which dissolves in water, and the hydrophobic tail formed by grafting of octadecyl isocyanate prefers to stay away from the water molecules. MKGM displays excellent emulsification properties, and it may be used along with commercial dispersants like Corexit to stabilize the dispersed oil droplets and thus warrants reduced quantity of dispersants used during the oil spill mitigation process. This application of MKGM can reduce the usage of the commercial dispersants, which are used in huge amounts during a major oil spill. The MKGM surfactant is bulky due to the long hydrophilic polymer chains, which makes the formation of monolayer at the air-water interface a slow process. It is also observed that the aggregation tendency of the polymeric structure of MKGM reduces the packing efficiency of the hydrophobic tail along the air-water interface resulting in minor reduction of surface tension of water, and making MKGM ineffective as a crude oil herder. However, the MKGM surfactant demonstrates oil herding on lighter oils like dodecane. The slowness to form monolayer and poor packing at air-water interface of MKGM may be resolved if the polymeric chain length of KGM can be reduced. The MKGM is showing dispersing abilities when demonstrated with crude oil, which gives scope for future research in developing environment friendly dispersants.

3. E-BEAM IRRADIATION OF KGM AND ITS EFFECT ON OIL HERDING EFFICIENCY

3.1. Summary

The effects of electron beam (e-beam) radiation on natural polysaccharides are well researched in the literature. The degradation mechanism of KGM by the chain scission of the polymeric chain is carried out by irradiating the KGM samples to radiation doses of 1.21 kGy, 5 kGy, 9kGy, and 16 kGy at the electron beam facility of Texas A&M. The long polymeric chain length is broken down using the e-beam. The Degraded KGM is then hydrophobically modified with the same method explained in chapter 2. The oil herding experiment with dodecane oil is carried out using the Degraded Modified KGM (DMKGM), and the results are compared with the non-degraded modified KGM. The oil herding is done in cold water (1°C) and at normal temperature water (22°C) to understand the effect of low temperature water on the oil herding. The possible reason for the increase in the oil herding efficiency due to the decreased polymeric chain length is discussed with the support of literature review.

3.2. Degradation of KGM using electron beam radiation

Zhenlin Xu et.al studied the effect of gamma irradiation on KGM. KGM was irradiated at 5, 20, 50, and 100 kGy, and its effect on some physicochemical properties were studied. The significant degradation of KGM was confirmed according to the reduction in the weight-average molecular weight (M_w). The degradation on KGM under gamma radiation was suggested due to the random chain scission of the KGM polymeric

backbone. The most reasonable degradation mechanism of KGM by gamma radiation was decided after studying the FT-IR and UV spectrum of the irradiated KGM. The FT-IR spectroscopy of degraded KGM suggests that no significant new chemical groups were introduced into the structure. The UV spectrum of irradiated KGM suggests the presence of carbonyl groups or double bond formed after the main chain scission of the polymer chain followed by the ring opening. The probable mechanism of the main chain scission of the polymer proposed by Zhenlin Xu et.al is shown in figure 3.1. (Zhenlin Xu, 2007)
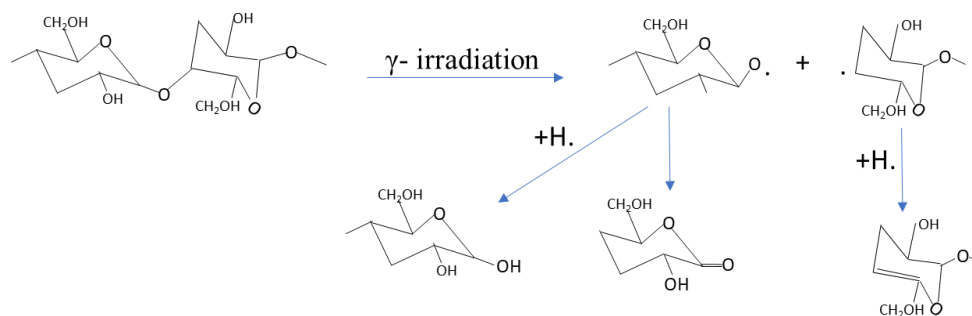
Figure 3-1: The probable degradation mechanism of KGM by γ-irradiation adapted with permission (Zhenlin Xu, 2007)

The degradation of KGM using gamma irradiation by chain scission of the main polymer chain encouraged us to consider irradiation of KGM samples to obtain shorter KGM polymeric chains. As discussed in Chapter -2, the ineffectiveness of MKGM surfactants to herd oil was assumed to be due to the extremely long polymeric backbone.

The irradiation method to break the polymer backbone of KGM was an encouraging way forward to understand the effect of having smaller hydrophilic polymer chains on oil herding.

Electron beam radiation is another method of irradiation that is gaining popularity and is considered as a competitive substitute for gamma radiation methods. The mode of interaction with the subject matter is similar in both the radiations. However, the differences are that electron beam can bring about a huge variation in the dose rate, precisely control the dosage, and subject the irradiated material to less exposure time. The electron beam radiation up to a limit of 20 kGy is observed to bring about similar physiochemical changes as compared to a gamma radiation. (Lecon Woo, 2002). So, it is assumed that the changes in the subject material is similar in both methods when the radiation dose is in lower ranges, in this case less than 20 kGy.

3.2.1. Irradiation of KGM at the electron beam facility at Texas A&M university

The electron beam facility of Texas A&M is under The National Center for Electron Beam Research (NCEBR) a leading academic and research organization focused on the research of Electron Beam (e beam). The facility has two 10 MeV 18 kW S-Band microwave-based linear accelerators with which the electrons are accelerated. The energies from these radiation sources do not induce any radioactivity in any material, including food. The high radiation safety standard followed in the facility was an encouraging factor in use of the facility for irradiating KGM.

3.2.2. E-beam irradiation material and method

3.2.2.1. Material and preparation

KGM purchased from Ticagel® Konjac High Viscosity TIC GUMS is vacuum dried for 24 hours and sample sets of 5 g are packed in a polyethylene bags of dimension 2 cm X 7.5 cm, which is placed inside another polyethylene bag of dimension 7.5 cm X 14 cm, as shown in figure 3.2.
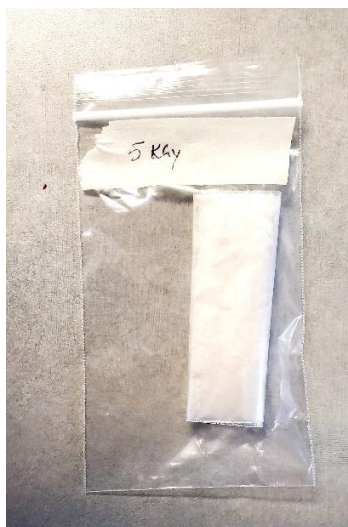
Figure 3-2: Vacuum Dried KGM (5 g) packed in polyethylene bag for e-Beam irradiation

3.2.2.2. E-beam irradiation method

The KGM samples are placed on the single conveyance system, which moves the sample through the process chamber where the electron beams are subjected on them, as shown in figure 3.3. The sample packet is attached with a radiation absorbing probe that

absorb the radiation along with the sample. These probes are used along with the calibrated readings to calculate the irradiation dose on the sample. The four samples are each irradiated to 1.21 kGy, 5 kGy, 9kGy, and 16 kGy.
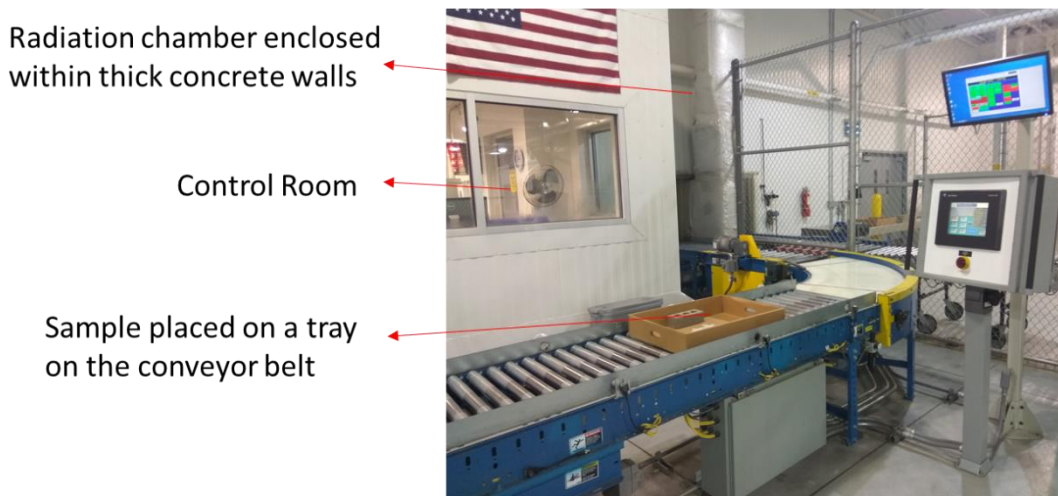
Figure 3-3: The e-beam facility setup in Texas A&M

3.3. Hydrophobic modification of degraded KGM

The degraded samples of KGM have undergone the hydrophobic modification, as described in section 2.2.2. The four samples of MKGM synthesized from the 1.21 kGy, 5 kGy, 9kGy, and 16 kGy irradiated KGMs are used for oil herding experiments to observe the effect of reducing the polymer chain length of the hydrophilic backbone of MKGM.

The oil herding experiment is repeated using the degraded MKGM (16kGy radiation dose), as described in section 2.4.1. The oil (dodecane) is observed to be retracting from its original shape due to the herding process. The dodecane applied on to

the water surface spreads out and stabilizes at time t = 0, then the degraded MKGM

(DKGM) surfactant is applied around the oil layer and the herding process photographs

are taken at time t= 15 min and then at time t= 30 min, as shown in figure 3.4.

| T= 0 min | T= 15 min | T = 30 min |
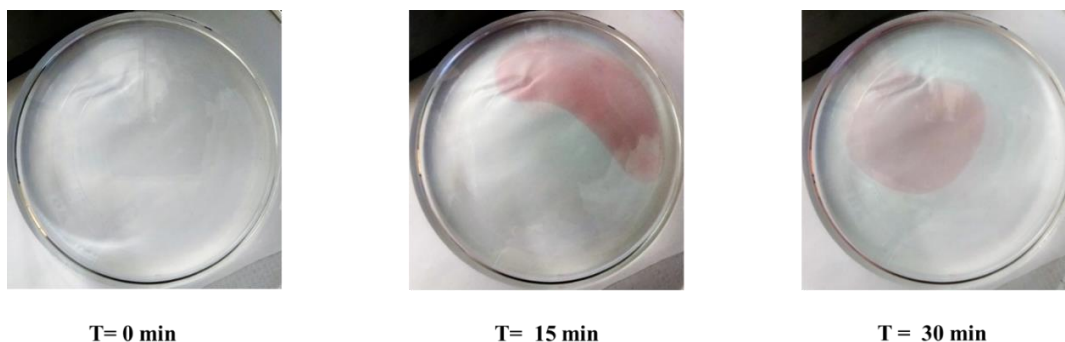
Figure 3-4: Oil herding using 16 kGy DMKGM

Clearly, it is observed that the degraded MKGM surfactant herds the same

quantity of dodecane in the same experiment setup in 30 minutes, whereas, the non-

degraded MKGM surfactant herded dodecane in 45 minutes. This result shows that

hydrophobic modification of degraded KGM results in a more effective oil herder. The

shorter hydrophilic polymer chain backbone may be causing a faster movement of the

diffused MKGM macromolecules to the water surface. Because the hydrophobic tails are

now attached to smaller polymeric backbone, it takes less time for the hydrophobic tails

to anchor to the non-polar phase, as shown in the figure 3.5(a). Additionally, the shorter

polymeric backbone has a lesser tendency to coil-in due to the attraction of hydrophobic

tails and thus prevent formation of aggregates that cause a smaller number of

hydrophobic tails to be arranged on the non-polar phase, as shown in figure 3.5(b).
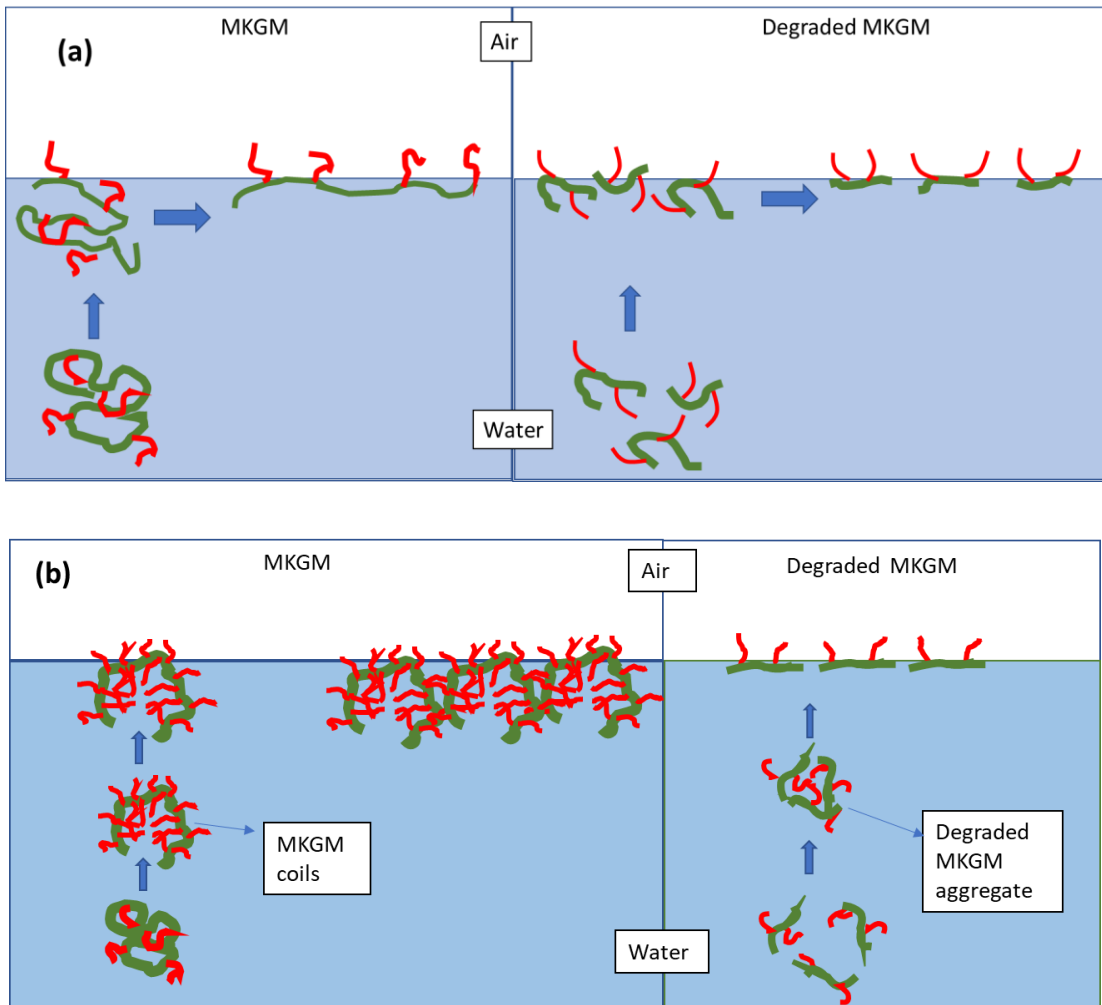
Figure 3-5: (a) The schematic comparing the arrangement of MKGM and degraded MKGM macromolecules along the air-water interface (b) The schematic comparing the coil-in tendency.

3.4. Oil herding experiment with degraded MKGM solution in toluene as delivering agent

The hydrophobic modification of DKGM is showing better herding efficiency, as shown in section 3.3. However, the herding process is slow compared to the surfactants like PEG monooleate (Polyethylene Glycol Monooleate), which takes less than 1 minute to form a stabilized retracted oil.

The oil herding experiment setup and the methodology followed is similar to that described in section 2.4.1. Normal temperature water (22° C) is taken in a Pyrex® 190 X 100 dish. The diameter and height of the dish is 190 mm and 100 mm, respectively. 0.4 ml red pigmented dodecane is carefully applied on the water surface using a transfer pipette and waiting till the oil has spread out and stabilized. Degraded MKGM (DMKGM) irradiated at 9 kGy is mixed with toluene (DMKGM/ toluene ratio 0.005 (wt/vol), and 0.4 ml of mixture is applied on the oil layer using a transfer pipette. Deeksha Gupta et. al had conducted herding experiment and used toluene as their herder carrying agent. (Deeksha Gupta, 2015)

The herding process images captured at regular intervals are shown in figure 3.6. It is observed that the dodecane retracts and stabilizes in 8 minutes. This is a drastic reduction in herding time compared to the previous herding experiments when the herder was dispersed in water solution. This improvement in the herding time may be due to the more efficient distribution of the DMKGM macromolecules. Since toluene is a non-polar liquid, applying on water the toluene would tend to float on the water surface reducing the DMKGM macromolecules interaction with water molecules. The DMKGM

macromolecules carried by toluene would then not tend to diffuse inside the bulk of the

water, but instead easily form a monolayer along the air-water interface reducing the

time taken for the macromolecules to align along the air-water interface.
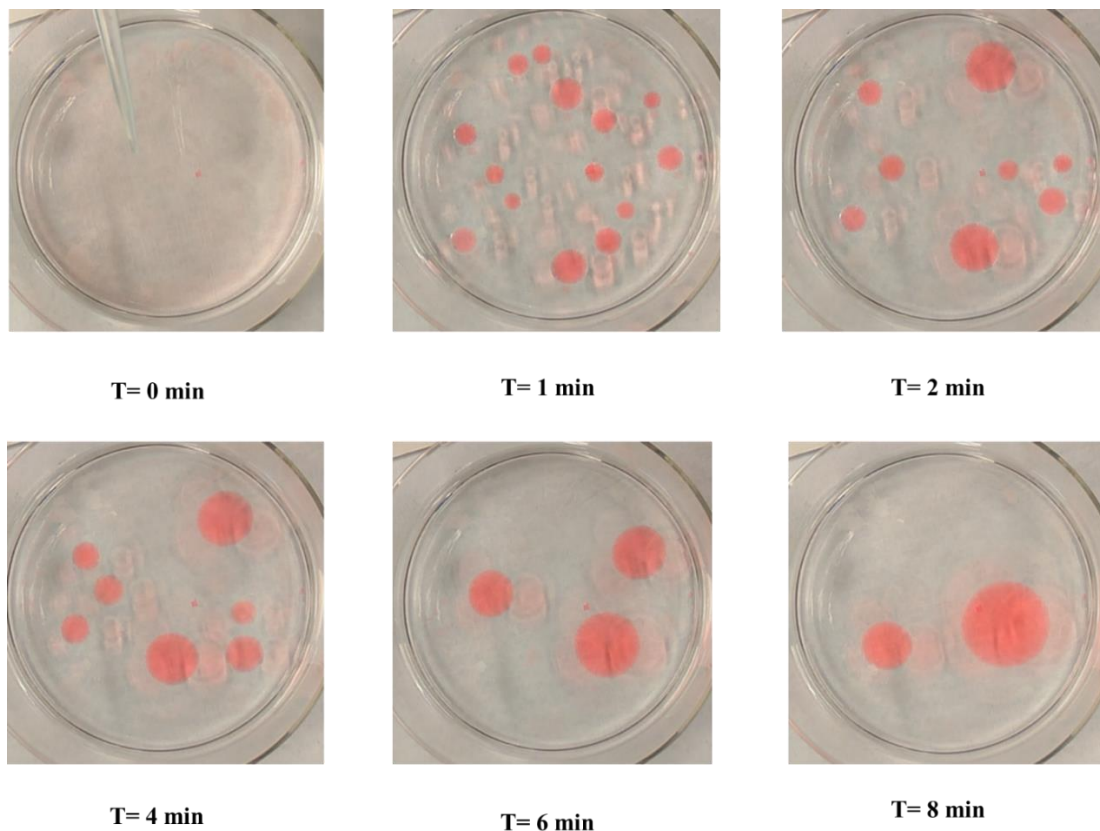
Figure 3-6: Oil herding using DMKGM in toluene - images captured at regular intervals till the herded oil is stable

3.5. Oil herding experiment with degraded MKGM in low temperature water

It would be interesting to know the oil herding ability of DMKGM in low

temperature water. To carry out this experiment, the water was cooled to 1° C using

Thermo Scientific, Neslab RTE 7, circulating bath, as shown in figure 3.7. The

methodology adopted is same as described in section 3.4. To compare the effect various

irradiation doses, the herding experiment was conducted with MKGMs irradiated to 1.21

kGy, 5 kGy, 9 kGy, and 16 kGy. It was observed that the herding time taken to herd oil

was more in cold water when compared to the normal water. In cold water (1°C) it took

10 minutes to herd the oil, whereas in the normal water the herding was completed in 8

minutes, when a 16 kGy DMKGM was used as the herding agent. This clearly shows

that at low temperature water the herding process is slow. (Deeksha Gupta, 2015)

Deeksha Gupta et.al states that the herding is slow at low temperature partly

because the oil and water viscosities increase in low temperature and the fluid motion is

more viscous.

Figure 3-7: Thermo Scientific, Neslab RTE 7, circulating bath

The behavior of MKGM macromolecules in the water and at the air-water interface may also vary with the temperature. However, it is encouraging that the MKGM surfactants are showing herding capabilities when water temperature is as low as 1° C.

The oil herding experiment of the DMKGM surfactants irradiated to 1.21 kGy, 5 kGy, 9 kGy, and 16 kGy were conducted and the time for the retracted oil to stabilize was noted. The result is shown in figure 3.8.
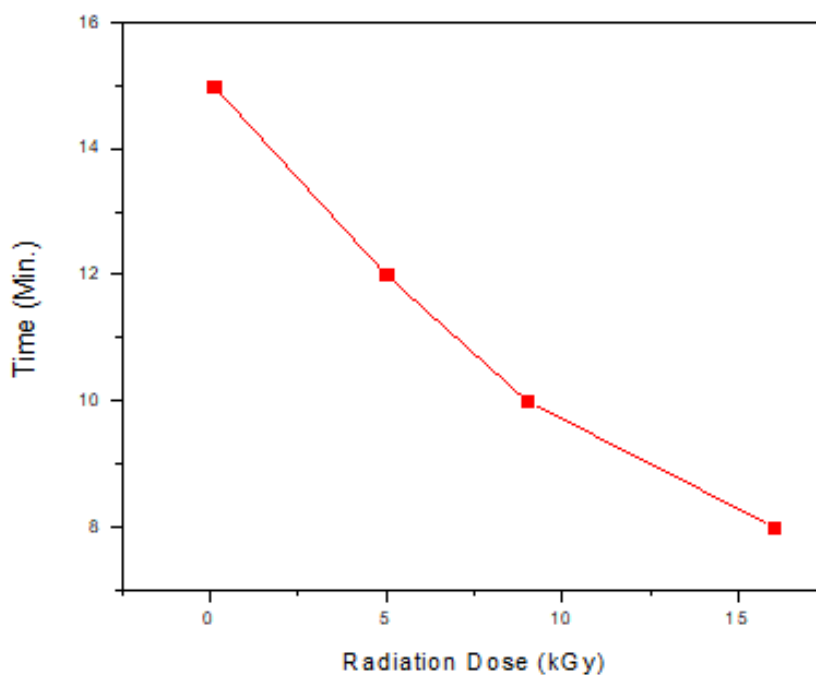
Figure 3-8: The comparison of herding time using DKGM irradiated to different doses

The graph in figure 3.8 clearly confirms that with the increase in the irradiation dose the oil herding time is reduced. This implies that the decrease in the hydrophilic

chain length increases the herding efficiency of the MKGM surfactant. The graph almost

shows a linear relationship between the radiation dose v/s time for herding.

This experiment is limited to the samples being irradiated to 16 kGy due to

restrictions at the electron beam facility of Texas A&M.

3.6. Measurement of surface tension using pendant drop tensiometer

Pendant drop tensiometry is a simple method to measure the surface and

interfacial tension of a surfactant solution. The process of fitting Young-Laplace

equation that balances the gravitational force acting on the liquid droplet against the

interfacial tension, which gives a typical axisymmetric fluid droplet forms the basis of

the technique followed. This method can measure the surface tension just by capturing

the shape of the liquid droplet suspended from the pendant drop needle using a camera

connected to a computer.

The pendant-drop experimental setup used for the calculation is shown in the

figure 3.9
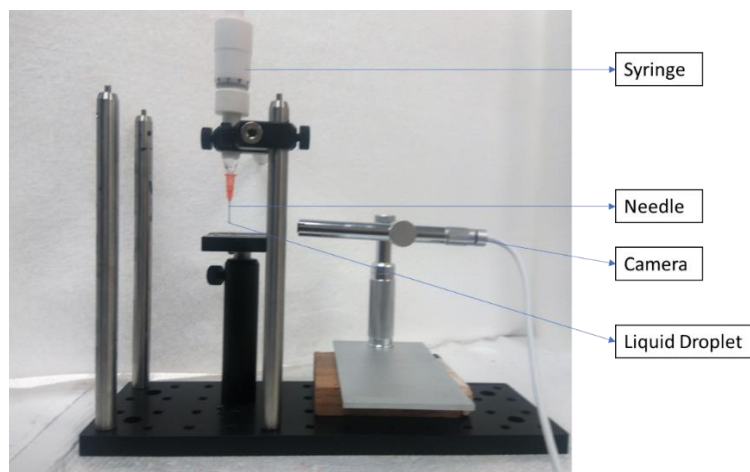
Figure 3-9: Pendant Drop surface tension measuring setup

The surface tension of pure DI water, hydrophobically modified KGM in water solution in ratio 0.05 (wt/vol), Degraded and hydrophobically KGM (16 kGy) in water solution in ratio 0.05 (wt/vol) was measured using the pendant drop method to compare the results.

The solution is first collected in the dispensing syringe and slowly the fluid is released to form a droplet. The fluid is released such that the maximum droplet size is achieved before it breaks to get the most accurate measurement. The droplet image is captured in the camera connected to the computer. A lamp is placed at the opposite side of the camera to give a shadowed image of the droplet in the camera, so that the image of outline of the droplet is captured perfectly. The software OpenDrop Master is used to calculate the surface tension, the captured image being the input to the software as shown in figure 3.10.
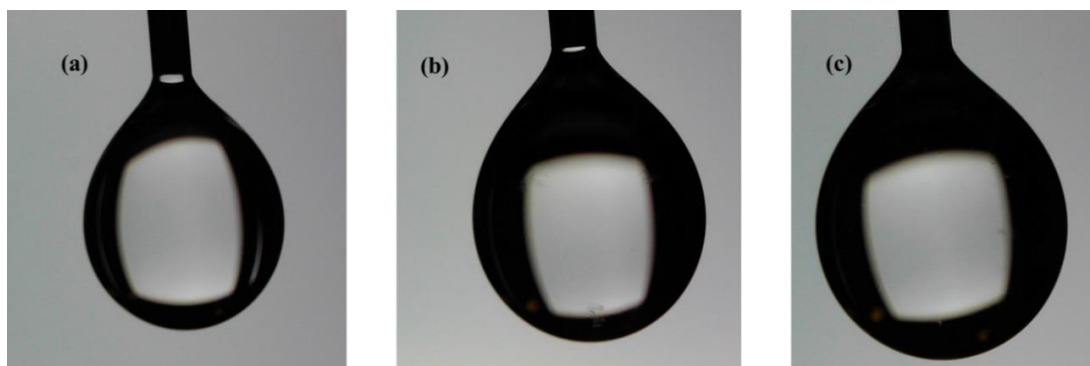
Figure 3-10: Profile of liquid droplets (a) Pure DI water (b) Hydrophobically modified KGM solution (c) Degraded and hydrophobically modified KGM solution

The surface tension for pure DI water, Pure KGM solution and Degraded and

hydrophobically modified KGM are 79.06 mN/m, 77.50 mN/m, and 77.18 mN/m.

It is concluded from the surface tension measurement that the hydrophobically modified

KGMs does not have a significant influence on interfacial tension.

3.7. Conclusion

The e-beam irradiation of KGM at doses of 1.21 kGy, 5 kGy, 9 kGy, and 16 kGy

and further hydrophobic modification of the degraded KGM resulted in surfactants with

different hydrophilic polymer chain lengths. The lab scale oil-herding experiments using

dodecane oil and the four different samples of surfactants illustrate that the decrease in

polymeric chain increases the efficiency of the oil-herding. This increase in oil-herding

efficiency may be due to faster monolayer formation at the air-water interface and more

efficient packing of the macromolecules resulting in denser hydrophobic tails

arrangement. The degradation of KGM did not show to have any negative impact on the

herding ability in low temperature water (1°C). Thus, e-beam degradation of natural

polysaccharides may be an exciting area to explore to functionalize biocompatible

surfactants for oil spill recovery mechanisms. Furthermore, e-beam irradiation is a safe

method and it does not have any harming effect in the irradiated product. The maximum

irradiation dose that could be achieved was 16 kGy for this research setup. However,

irradiation doses in the range of 50 kGy to 100 kGy will cause more degradation, and it

may be interesting to understand the improvement in oil-herding when KGM is

subjected to higher doses. Using toluene as the solvent for releasing the surfactants the

time taken to herd the oil improves when compared to discharging surfactant using water

as solvent. This may be due to the faster and efficient distribution of surfactant macromolecules on the air-water interface. The measurement of surface tension of pure DI water, MKGM solution and DMKGM solution shows that the interfacial influence of KGM based surfactants is not high enough to use them as oil herders in an efficient manner.

4. THE RELATIONSHIP OF MKGMs KRAFFT TEMPERATURE AND ITS EFFECTIVENESS IN HERDING OIL IN LOW TEMPERATURE WATER

4.1. Summary

The Krafft Temperature (T_k) and the Critical Micelle Concentration (CMC) are specific characteristics that define the properties and application of surfactants. It is important to note that surfactant's application should be above its T_k, because the surfactant loses its unique properties below T_k. When considering the using surfactants as oil herders, it is vital to realize that the application of surfactants above CMC does not make any difference in its performance, and thus it is inefficient to disperse oil herders above its CMC. It is demonstrated in chapter 3 that the KGM based oil herders are not affected by low temperature water. To understand the behavior of KGM based surfactants in low temperature water, the solubility of it in water with varying temperature was investigated. By measuring the conductivity of the surfactant in water solution with varying temperature, the solubility of the same is understood. The T_k and CMC can be determined by examining the conductivity v/s temperature trend. The conductivity v/s temperature trend of ionic surfactant – Sodium Dodecyl Sulfate (SDS) and non-ionic surfactants MKGM and PEG Monooleate were studied. The comparison of behavior of both ionic and non-ionic surfactants in varying water temperature is described in this paper.

4.2. Ionic surfactant behavior in water solution with varying temperature

The understanding of the behavior of generic surfactant(amphiphile) with a typical structure, as show in figure 4.1 (a), when diffused in water does not take into consideration various complexities like the surfactant structure, chemical composition, presence of electrolyte, role of counterions, etc. Amphiphiles when diffused in water, reorient themselves in the most thermodynamically favorable position. The dual nature of the amphiphile with both the attraction and repulsion with water molecules forces them to orient themselves such that the hydrophobic tail (water hating section) has the least contact with water. This behavior forces the amphiphiles to adsorb at the air-water interface with the hydrophobic tail on the air side, resulting in formation of a monolayer as shown in figure 4.1 (b). When the saturation level has attained at the air-water interface, the further addition of the amphiphiles tends to aggregate together such that the hydrophobic tails are in least contact with the water molecules leading to the formation of aggregates called micelles, as shown in figure 4.1 (c). The aggregates can take any shape, like the spherical, lamellar, cylindrical, etc. The specific concentration at which the micelle formation begins is called the Critical Micelle Concentration (CMC). Below CMC, the monomers added to the solution stays as monomers and may form monolayers, as shown in figure 4.2 (d). (Myers, 2006)

(a)

Hydrophilic Head

Hydrophobic Tail

(b)

Air

Monolayer

Water

(c)

Air
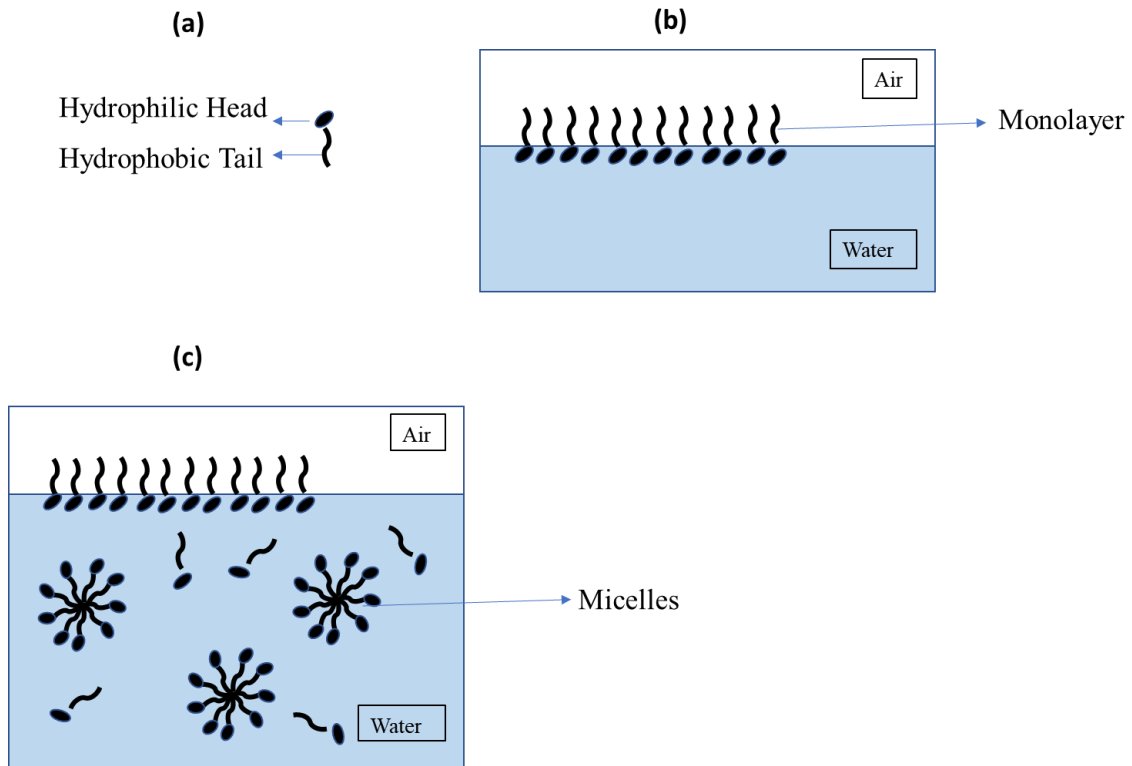
Micelles

Water

Figure 4-1 Behavior of generic surfactant(amphiphile) in water. (a) Generic surfactant structure (b) Surfactants forming monolayer at air-water interface (c) Formation of micelles

The impact of temperature on the surfactant solubility in water is significant with regards to this research. In a fixed monomer concentration (above its CMC) when the temperature is varied, the solubility of monomers changes based on the physical structure they form in the water. For ionic surfactants, the overall solubility increases with temperature. When temperature is low, the monomers crystallize and basically act as solid phase inside the water. This solid phase is also described as the hydrated crystal as shown in figure 4.2 (a). The hydrophobic tail freezes at this temperature range, losses its property, and acts as a solid. On gradual raise of temperature, the crystal lattice energy is surpassed, and the system thermodynamically favors the conversion of the

crystal lattice to micelles, as shown in figure 4.2 (b), which results in increased solubility in water. The temperature or temperature range at which there is drastic increase in solubility with a relatively small increase in temperature is called the Krafft Temperature (T_k) (Tanaka, 2004) (Hirotaka Hirata, 1996). T_k is a critical temperature point of a surfactant because, below this temperature, the surfactant will lose its surfactant property and cannot be used for any applications. Any addition of monomers into the solution below T_k will not result in formation of monolayer or micelles, as shown in figure 4.2 (a and c). So, it is crucial to ensure that the temperature of the intended application of surfactant is above its T_k.
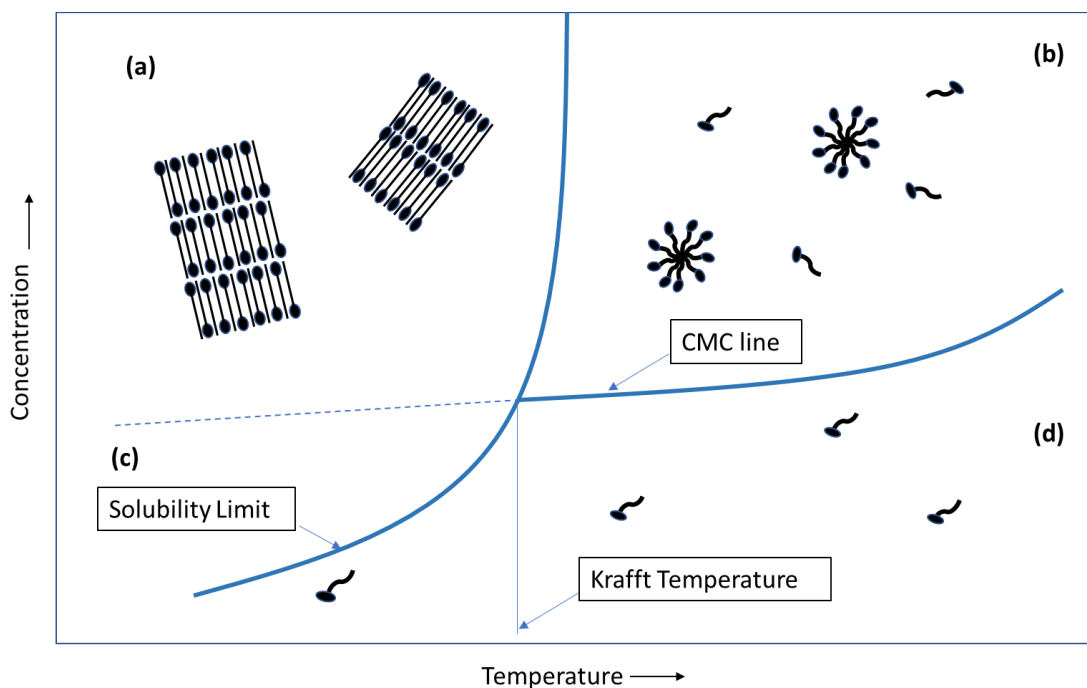
Figure 4-2: Schematic of a typical ionic surfactant phase diagram (Iwata, 2017)

When designing a surfactant for oil herding it is vital to understand both the T_k and the CMC of the surfactant, because below T_k the surfactants will not dissolve in the water and form monolayers and micelles, and any concentration of surfactant above CMC will result only in additional micelles in the system, which will not have any impact on the surface tension of the water. This is because at this concentration the monomers have already saturated the air-water interface forming the monolayer and additional monomers will form micelles.

The solubility and micellization of ionic surfactants depend largely on the ionic bonding between the charged hydrophilic head, the polar water molecules, and many other factors. The nonionic surfactants follow opposite temperature - solubility trend, that is, the solubility decreases with increase in temperature.

4.3. Non-ionic surfactant behavior in water solution with varying temperature

Non-ionic surfactant/water solution at a concentration (above CMC) when heated at a steady rate experiences decrease in solubility in water. That is to say the non-ionic surfactants do not have a T_k. Instead a phase separation occurs as temperature increases in non-ionic surfactants resulting in a turbid appearance at a temperature called the "cloud point". (Vladimir Aseyev, 2010)

The hydrophilic head of the surfactant starts to lose its bond with water molecules as the temperature increases. These hydrophilic head groups that become less polar, interact less favorably with water, and more favorably with themselves, leading to a tighter packing of the hydrophilic groups and an increased tendency to phase-out from the solvent. (Krister Holmberg, 2002)

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This tighter packing of hydrophilic polymer chain results in coil-in of the surfactant structure, as shown in figure 4.3. As the more and more hydrates are released from the hydrophilic part, the surfactant structure collapses within and eventually becomes completely separated from the water solution. So clearly, the solubility of non-ionic surfactants decreases with increase in temperature.
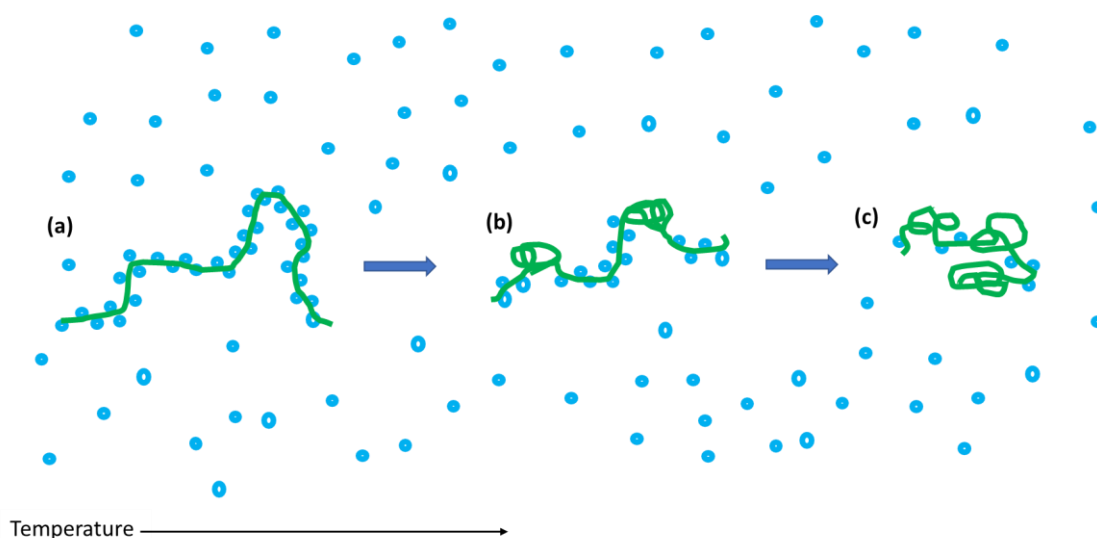
Figure 4-3: Schematic of non-ionic surfactant behavior in water with increase in temperature. (a) The hydrophilic head (green color) attracts the water molecules (blue color) (b) As temperature increases the water molecules are released from the hydrophobic polymer chain and tend to coil-in (c) The hydrophobic polymer chain coil-in and collapse causing them to phase out of water solution

4.4. Determination of krafft point by measurement of conductivity

The micellar aggregation theory of surfactant solution has a close relation to its solubilization. Hirotka Hirata has shown that measuring the conductivity of the solution is a proven method to identify the Krafft Temperature and CMC of a given surfactant solution (Hirotaka Hirata, 1996). The conductivity measurement of ionic surfactant -

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SDS (Sodium Dodecyl Sulfate) and non-ionic surfactants DMKGM and PEG-Monooleate are conducted to understand the behavior of these surfactant solutions in water with varying temperature.

4.4.1. Materials and method

The materials used are Sodium Dodecyl Sulfate (SDS), Degraded Modified Konjac Glucomannan (DMKGM) synthesized as described in section 3.3 and 2.2.2, and PEG-monooleate (Aldrich). The hand-held conductivity/TDS meter CON 6/TDS 6 of Oakton instruments was used to measure the conductivity and the temperature of the sample.

4.4.2. Conductivity measurement of SDS

First, 200 ml of SDS in DI water solution of 0.1 mol/l concentration was prepared in a 200 ml glass beaker. The solution was left in a refrigerator at 5°C for 24 hours. This process has brought about the crystallization of the surfactant. The glass beaker is taken out of the refrigerator and placed on a hot plate stirrer (CORNING PC-420). The probe stick of the conductivity meter (TDS meter CON 6/TDS 6) is inserted into the solution. The dual measuring mode of conductivity meter can measure both the conductivity and the temperature. The setup is shown in figure 4.4. The conductivity of the solution is recorded from 12°C and measured till 28°C. The solution is slightly heated to attain a steady temperature rise. The conductivity is measured at regular intervals of temperature (0.2^{o}C raise) and noted down. The whole process takes about 2.5 hours. The results of the experiment are recorded in Table 1. The conductivity (mS) v/s Temperature (^{o}C) is plotted as shown in figure 4.5.

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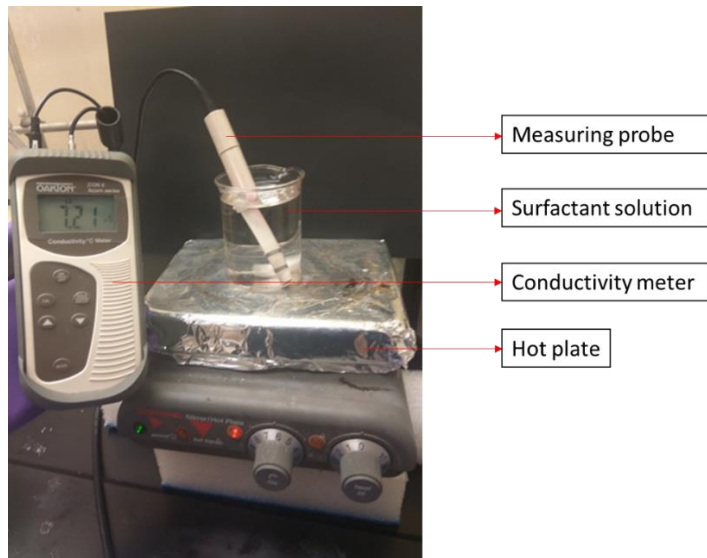
Figure 4-4: The experimental setup for measuring conductivity
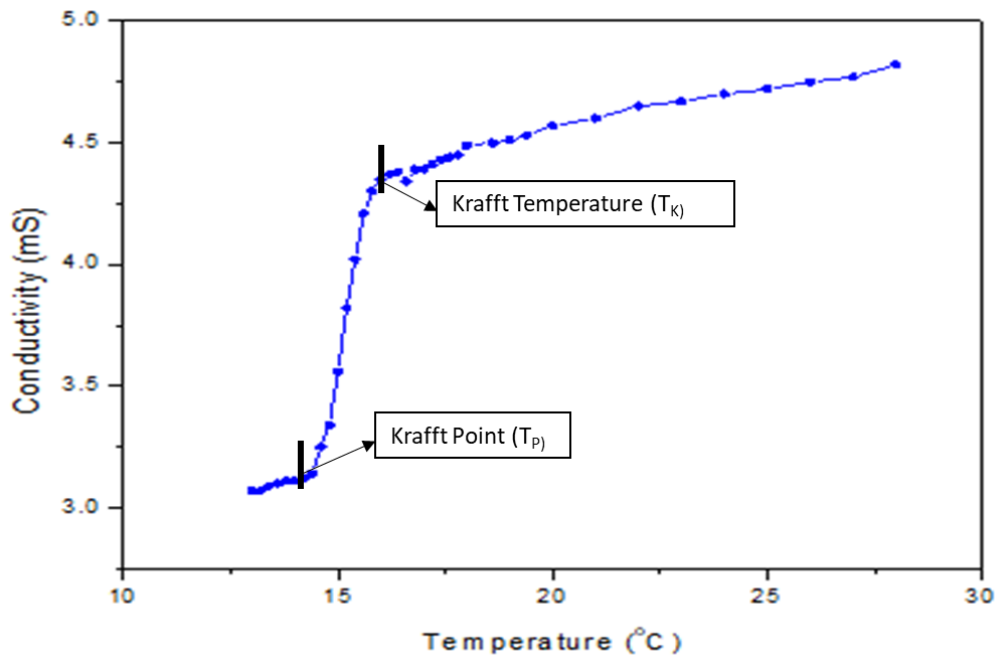
Figure 4-5: Conductivity(mS) v/s Temperature (ºC) graph for 0.1 mol/L SDS solution (ionic surfactant) in water

There is increase in conductivity with increase in temperature. Initially, the rate

of increase in conductivity is slow, from 13ºC to 14.4ºC, and then there is abrupt

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increase in conductivity marked as Krafft Point (T_p) in figure 4.5, where the monomer solubility is equal to the critical micelle concentration (CMC). The rapid increase in conductivity is aided by the micelles formed by the monomers, which are de-crystalized. The conductivity increase attains a steady rate, marked as Krafft Temperature (T_k), which corresponds to 16.2°C. Beyond T_k, the monomers continue to form more micelles causing a slow increase in conductivity. It is to be noted that this phenomenon of abrupt increase in conductivity can be observed only if the concentration of the surfactant solution is above its CMC.

The surfactant molecular arrangement changes with the temperature resulting in changes in the conductivity of the solution which is shown in figure 4.6 for an ionic-surfactant.
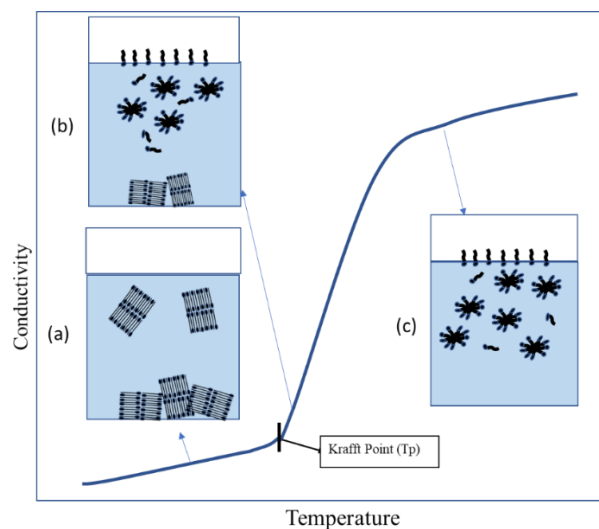
Figure 4-6: Schematic of Conductivity v/s Temperature with molecular arrangement for ionic-surfactants

Figure 4.6 (a) shows the crystallized monomers of the ionic-surfactants below the Krafft point (T_p). Figure 4.6 (b) shows the formation of micelles when the T_p is crossed and the micelles increasing the conductivity of the solution. Figure 4.6 (c) is the additional formation of micelles causing a steady increase in conductivity.

The conductivity v/s temperature graph of the ionic-surfactant solution shows that below the Krafft temperature (T_k) the ionic-surfactant crystallizes and does not pose any surfactant related properties. So ionic-surfactants will be useful only when its application is above T_k.

4.4.3. Conductivity measurement -of degraded modified KGM

First, 0.25 % (w/w) of 200 ml of Degraded Modified KGM (DMKGM) (irradiated to 16 kGy) with water solution is placed in a refrigerator for 24 hours to bring the temperature to 0°C. The measurement of conductivity is carried out as mentioned in section 4.5.2. The conductivity is measured at regular intervals of temperature and noted down. The whole process took about 3 hours. The results of the experiment are recorded in Table 2. The conductivity (µS) v/s Temperature (°C) is plotted as shown in figure 4.7. It is clear from the figure 4.7 that there is a steady decrease in the conductivity of the solution when temperature is increased. Unlike SDS, DMKGM does not show any abrupt increase in conductivity and does not appear to have a Krafft temperature.

This phenomenon can be explained with the behavior of non-ionic solutions with temperature as discussed in section 4.4. The decrease in the conductivity can be traced to the decrease in solubility of DMKGM in water as temperature increase, as shown in figure 4.8.

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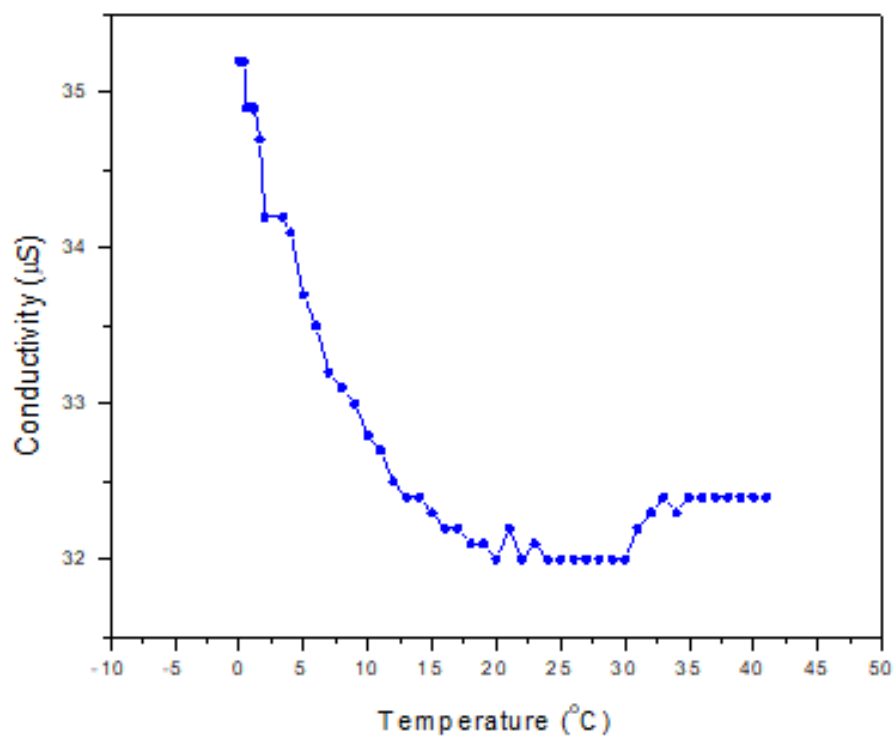
Figure 4-7: Conductivity (µS) v/s Temperature (°C) graph for 0.25 % (w/w) DMKGM in water solution (non-ionic surfactant)
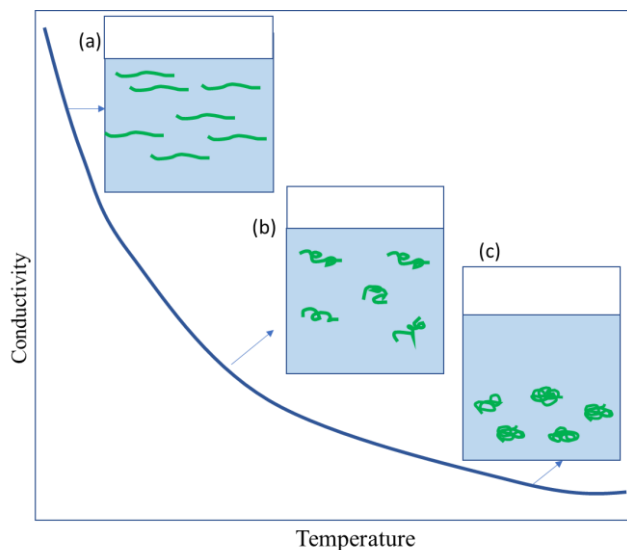
Figure 4-8: Schematic of Conductivity v/s Temperature with the molecular arrangement of non-ionic surfactants

4.4.4. Conductivity measurement of poly ethylene glycol monooleate (PEG Monooleate)

PEG Monooleate is also a non-ionic surfactant and the conductivity v/s temperature of this surfactant in water at 0.1 mol/L concentration was conducted, as described in section 4.5.2. In this experiment the sample was first cooled to 2.7°C and then the increase in conductivity was noted up to 30°C. The same sample was cooled by applying ice around the 250 ml glass beaker as shown in figure 4.8, and the conductivity was recorded till the temperature dropped to 5°C. The conductivity v/s temperature graph is, as shown in figure 4.9. The results clearly show that for non-ionic surfactants the solubility decreases with increase in temperature and it is a reversible process, that is, the solubility increases with decrease in temperature.
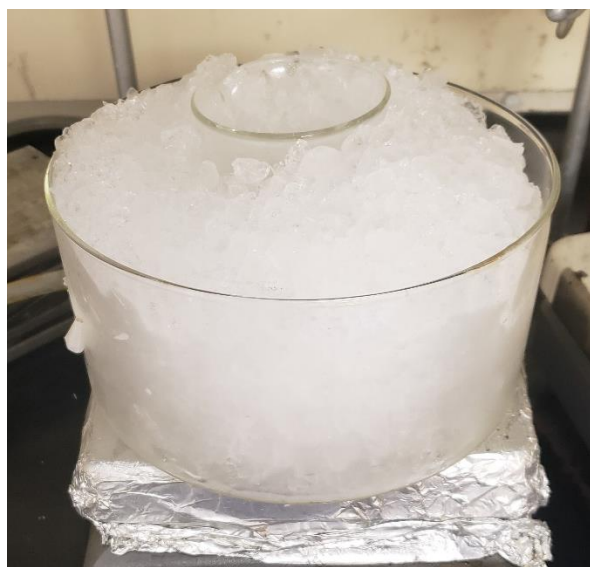
Figure 4-9: Cooling PEG-Monooleate- water solution using ice packing
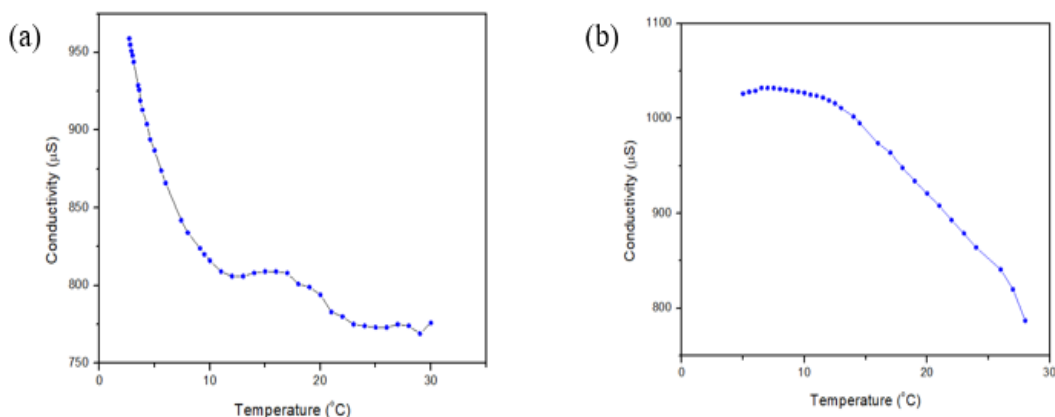
Figure 4-10: The conductivity v/s temperature graph for 0.1 mol/L of PEG monooleate in water solution (non- ionic surfactant) (a) Temperature increased from 2.7ºC to 30ºC (b) Temperature decreased from 30ºC to 5ºC

4.5. Conclusion

The comparison on the solubility behavior of ionic surfactant -SDS with the non-ionic surfactants – MKGM and PEG monooleate shows that the they both display opposite behavior when the temperature in varied. The ionic surfactants clearly show an increase in the solubility as temperature increases and is characterized by a sudden increase in conductivity when the temperature attains the Kraft Temperature (T_k). However, for non-ionic surfactant MKGM the conductivity decreases with increase in temperature explaining the absence of T_k for MKGM surfactant. This absence of T_k gives MKGM surfactant ability to retain its surfactant ability at low temperature nearing 0ºC and opens its way to act as oil herders for low temperature waters, especially for oil spills in Arctic waters.

5. CONCLUSION

The hydrophobically modified KGM surfactant demonstrates oil herding capabilities on lighter oils like dodecane. The e-beam irradiation of KGM at doses of 16 kGy and hydrophobic modification of the degraded KGM resulted in surfactants with shorter hydrophilic polymer chain lengths. The lab scale oil-herding experiments using dodecane oil illustrate that the reduction in polymeric chain increases the efficiency of the oil-herding. This increase in oil-herding efficiency may be due to faster monolayer formation at the air-water interface and more efficient packing of the macromolecules resulting in denser hydrophobic tails arrangement. The degradation of KGM did not show to have any negative impact on the herding ability in low temperature water (1°C). Thus, e-beam degradation of natural polysaccharides may be an exciting area to be explored to functionalize biocompatible surfactants for oil spill recovery mechanisms. Furthermore, e-beam irradiation is a safe method and it does not have any harming effect in the irradiated product. The measurement of surface tension of Modified KGM surfactant solution shows that the interfacial influence of KGM based surfactants is not high enough for them to be used as oil herders in an efficient manner. However, the influence of e-beam degradation of KGMs to higher doses in improving the herding efficiency is a promising observation.

Modified KGM surfactant is non-ionic and is experimentally determined not to have a Krafft Temperature (T_k). The absence of T_k gives Modified KGM surfactant unique ability to retain its surfactant ability at low temperature nearing 0°C and opens its

way to act as efficient oil herders for low temperature waters, especially for oil spills in Arctic waters.

5.1. Future areas of research

1. The hydrophobic modification was performed using octadecyl isocyanate and 1,3-Propane Sultone. It would be interesting to find out if hydrophobic functionalization can be done using other chemicals, which could improve the oil-herding abilities of KGM

2. The e-beam irradiation dose was restricted to 16 kGy in this research paper. KGMs are capable of handling e-beam irradiations of the range 300 kGy. There is a tremendous scope to explore the effect of higher e-beam irradiation doses on the properties of KGM, which are suitable for oil-herding.

3. Research on the usage of modified KGM as oil dispersant stabilizers is a promising field of application. Modified KGM displays an excellent emulsification property and it may be used along with commercial dispersants like Corexit to stabilize the dispersed oil droplets and therefore warrants reduced quantity of dispersants during oil spill mitigation process. This application can reduce the usage of the commercial dispersants which are used in huge amounts during a major oil spill.

4. Research on the application of modified KGM as dispersants is also a possible area to ponder. Modified KGM is showing dispersing abilities when demonstrated with crude oil in a lab-scale setup, which gives scope for future research in developing environment friendly dispersants.

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APPENDIX A

CONDUCTIVITY MEASUREMENT TABLES

Table 1: The Conductivity measurement at different temperatures for SDS (0.1 mol/L) in water

Sn.	Temperature (^oC)	Conductivity (mS)
1	13	3.07
2	13.2	3.07
3	13.4	3.09
4	13.6	3.1
5	13.8	3.11
6	14	3.11
7	14.2	3.12
8	14.4	3.14
9	14.6	3.25
10	14.8	3.34
11	15	3.56
12	15.2	3.82
13	15.4	4.02
14	15.6	4.21
15	15.8	4.3
16	16	4.35
17	16.2	4.37
18	16.4	4.38
19	16.6	4.34
20	16.8	4.39

Sn.	Temperature (^oC)	Conductivity (mS)
21	17	4.39
22	17.2	4.41
23	17.4	4.43
24	17.6	4.44
25	17.8	4.45
26	18	4.49
27	18.6	4.5
28	19	4.51
29	19.4	4.53
30	20	4.57
31	21	4.6
32	22	4.65
33	23	4.67
34	24	4.7
35	25	4.72
36	26	4.75
37	27	4.77
38	28	4.82

Table 2: The Conductivity measurement at different temperatures for DMKGM (0.25% (w/w)) in water

Sn.	Temperature (°C)	Conductivity (µS)
1	0	35.2
2	0.4	35.2
3	0.6	34.9
4	0.8	34.9
5	1	34.9
6	1.2	34.9
7	1.6	34.7
8	2	34.2
9	3.4	34.2
10	4	34.1
11	5	33.7
12	6	33.5
13	7	33.2
14	8	33.1
15	9	33
16	10	32.8
17	11	32.7
18	12	32.5
19	13	32.4
20	14	32.4
21	15	32.3
22	16	32.2

Sn.	Temperature (°C	Conductivity (µS)
23	17	32.2
24	18	32.1
25	19	32.1
26	20	32
27	21	32.2
28	22	32
29	23	32.1
30	24	32
31	25	32
32	26	32
33	27	32
34	28	32
35	29	32
36	30	32
37	31	32.2
38	32	32.3
39	33	32.4
40	34	32.3
41	35	32.4
42	36	32.4
43	37	32.4
44	38	32.4
45	39	32.4
46	40	32.4
47	41	32.4