

**pH-SWITCHABLE DYNAMIC BINARY COMPLEXES
AS VISCOSITY MODIFYING AGENTS**

A Thesis

By

BHARGAVI SRIPATHI BHAT

Submitted to the Office of Graduate and Professional Studies of
Texas A&M University
in partial fulfilment of the requirements for the degree of

MASTER OF SCIENCE

Chair of Committee,
Committee Members,

Head of Department,

Mustafa Akbulut
Victor Ugaz
Emily Pentzer
Arul Jayaraman

December 2020

Major: Chemical Engineering

Copyright 2020 Bhargavi Bhat

ABSTRACT

The study of supramolecular structures has been gaining a lot of momentum in recent years due to their potential application in several interesting areas such as medicine, catalysis, energy, oil and gas, etc. Hydraulic fracturing is one area where the ongoing demand for novel viscosity modifiers has prompted researchers to explore various facets of chemistry. In this study, a dynamic binary complex (DBC) solution is presented, with the potential to be useful in the hydraulic fracturing domain. It has a supramolecular structure that is formed by the self-assembly of oleic acid and diethylenetriamine into an elongated network under alkaline conditions. With less than 2 wt% of constituents in aqueous solution, a viscous gel that exhibits high viscosities even under shear was formed. It was sensitive to pH and salinity, and its zero-shear viscosity could be tuned by a factor of ~ 280 by changing the pH. Furthermore, its viscous properties were pronounced in the presence of salt. Sand settling tests revealed its potential to hold up sand particles for extended periods of time, longer than 24 hours. In conclusion, this DBC solution system has potential to be utilized as a smart pH-switchable hydraulic fracturing fluid that can be prepared using seawater.

ACKNOWLEDGEMENTS

I would like to thank my advisor, Dr. Mustafa Akbulut for his constant guidance throughout the course of this research. I would also like to thank Dr. Victor Ugaz and Dr. Emily Pentzer for serving on my committee.

I am also extremely grateful to my colleagues in my research group for guiding me and helping me pick up the skills required to conduct this research. I also appreciate the Department of Chemical Engineering at Texas A&M University for giving me this platform to learn and grow.

Finally, I wish to express my deepest gratitude to my family members who have always supported me and motivated me towards my goals.

NOMENCLATURE

pH	Potential of Hydrogen
Wt%	Weight Percentage
cP	Centi-Poise
Pa	Pascals
hr	Hours
min	Minutes
DBC	Dynamic Binary Complex
PAM	Polyacrylamide
CTAB	Cetyltrimethylammonium Bromide

CONTRIBUTORS AND FUNDING SOURCES

Contributors

This work was supervised by a committee consisting of Professor Mustafa Akbulut [Principal Advisor] and Professor Victor Ugaz of the Department of Chemical Engineering and Professor Emily Pentzer of the Department of Material Science and Engineering. All the data collection and work for this thesis was completed independently by the student.

Funding Sources

This project was funded by a grant obtained from the Department of Energy (DOE) with project title “Dynamic Binary Complexes as Super-Adjustable Viscosity Modifiers for Hydraulic Fracturing Fluids”.

TABLE OF CONTENTS

	Page
ABSTRACT.....	ii
ACKNOWLEDGEMENTS.....	iii
NOMENCLATURE	iv
CONTRIBUTORS AND FUNDING SOURCES	v
TABLE OF CONTENTS.....	vi
LIST OF FIGURES	viii
1. INTRODUCTION	1
1.1 Hydraulic Fracturing Fluids	1
1.2 Micelles and Supramolecular Structures.....	3
1.3 Scope and Objective of this Thesis	5
2. MATERIALS AND METHODS.....	9
2.1 Materials and Sample Preparation.....	9
2.2 Rheological Measurements	9
2.4 Sand Settling Test.....	10
2.5 Microscopy Analysis.....	10
3. RESULTS AND DISCUSSION	11
3.1 Sensitivity to pH.....	11
3.2 Viscoelastic Test Results.....	14
3.3 Effect of Salinity	15
3.4 Sand Settling Test.....	17
3.5 Microscopy Results and Microstructure	20
3.6 Application Potential.....	22

4. FUTURE WORK.....	23
4.1 Different Long-Chain Compounds.....	23
4.2 Different Complexing Agents	25
5. CONCLUSION.....	26
REFERENCES	27

LIST OF FIGURES

	Page
Figure 1: Mechanism of formation of entangled networks in solution by Dynamic Binary Complexes.....	6
Figure 2: (a) Structure of Oleic Acid, (b): Structure of Diethylenetriamine	8
Figure 3: Viscosity variation with pH of (a) 1 wt% DBC solution + 3 wt% NaCl, (b) 2 wt% DBC solution + 1 wt% NaCl. The error bars indicate the standard deviation.....	12
Figure 4: Zero Frequency Viscosity Comparison between 2 wt%, 1 wt% Polyacrylamide(PAM) solution and 2 wt%, 1 wt% Dynamic Binary Complex(DBC) solution. All the solutions contain 3 wt% NaCl. The error bars indicate standard deviation.	13
Figure 5: Storage (G') and loss (G'') moduli of 2wt% DBC+3wt% salt at (a)pH 9, (b)pH 10, (c)pH 11, (d)pH 12. The error bars indicate standard deviation	14
Figure 6 : Effect of Salinity on the Viscosity of 2 wt% DBC at pH 11.....	16
Figure 7: Sand Settling Test for (a) 1 wt% DBC + 1 wt% salt at room temperature (23°C) (b) 1 wt% DBC + 3 wt% salt at room temperature (23°C)	17
Figure 8 : Sand settling test at 90°C of 2 wt% DBC + 3 wt% salt.....	19
Figure 9: Optical microscopy images (30x magnification) of solutions at (a) pH 9 and (b) pH 11	20
Figure 10: Mechanism for synthesis of amidosulfobetaine compounds.....	24

1. INTRODUCTION AND LITERATURE REVIEW

1.1 Hydraulic Fracturing Fluids

In a swiftly expanding world, the demand for energy and resources have been steadily increasing. Traditional crude oil is a finite non-renewable resource and its reserves are not considered sufficient to meet the ever-increasing demand (Miller and Sorrell, 2004; Owen et al., 2010). In an effort to mitigate the lack, focus has shifted towards the production of shale throughout the world. This has led to an increased focus on hydraulic fracturing to extract shale gas in unconventional reservoirs (Wang and Krupnick, 2015). Before the hydraulic fracturing boom, it was uneconomical to consider extraction from these reservoirs (Jasechko and Perrone, 2017). The fracturing fluid used in the process plays a crucial role in determining the efficacy of the process, and must be selected carefully based on the rock formation and output requirements (Chen et al., 2014). It usually consists of a large amount of water, with several additives that behave as viscosity modifiers, biocides, scale inhibitors, iron-reducing agents, friction reducers, etc (Blauch, 2010; Loveless et al., 2011). Also, it is crucial that the fracturing fluid mixture has sufficient viscosity to transport proppant (sand particles) effectively to create fractures in the formations (Hu et al., 2015). The process itself involves pumping the fracturing slurry at a high pressure to propagate fractures in the reservoir, which serve as conductive paths for shale gas to flow out of the reservoir and in to the wellbores (Siddhamshetty et al., 2020, 2018).

Fracturing fluids, which have been documented for several years on a commercial scale can be broadly divided into a few categories guar/polymer-based fluids (linear and crosslinked gels); slickwater; viscoelastic surfactant based fluids (VES fluids); and

foam based fluids (Barati and Liang, 2014; Fu and Liu, 2019). Each of these categories come with their own set of merits and demerits. Though fluids based on guar gum and its derivatives account for about 90% usage due to their low cost and adequate rheological characteristics, the severe damage it causes to the reservoir (i.e., called formation damage) is a major area of concern (Hasan and Abdel-Raouf, 2018; S. Wang et al., 2019). There has been movement towards the use of slickwater to combat some of the issues associated with traditional linear or crosslinked gels. It is a water-based fracturing fluid with a small amount of friction reducer such as a high molecular weight polypropylene (Wang et al., 2020). However, its low viscosity and subpar proppant carrying capability have been considered as a major drawback (Palisch et al., 2010). Another variety available is foam based fracturing fluids, which are formed by adding pressurized gas, usually CO₂ or N₂ to water-based or oil-based gels (Castro Dantas et al., 2005). They can contain up to 95% gas and are thus preferred because of their low water requirement, but are limited in application due to complications arising from high costs and logistical issues (Wanniarachchi et al., 2017; Yekeen et al., 2018). Viscoelastic surfactant fluids have been a step towards achieving clean fracturing fluids with internal breaking properties, such that they can be reused (X. Yang et al., 2019a). They form elongated wormlike micelles in solution which entangle and form a network to yield increased solution viscosity (Hoffmann, 2003). Some of their key drawbacks include insolubility under saline conditions and high leak off rates (Hull and Sayed, 2016; Whitlock et al., 2015). The addition of nanoparticles has been experimented with for almost all types of hydraulic fracturing fluids in order to overcome some of their characteristic drawbacks (Al-Muntasheri et al., 2017; Yekeen et al., 2019). Another alternative to improve the properties of fracturing fluids is the use of supramolecular complex based fluids, which have received much attention recently (Jiang et al., 2016;

Yang et al., 2016; Yegin et al., 2016). Apart from the type of fluid used, there has also been a growing interest in discovering ways by which seawater can be used rather than groundwater for these fracturing processes to improve its ecological viability (Abdul Majid et al., 2017).

1.2 Micelles and Supramolecular Structures

Surfactants are amphiphilic molecules that consist of a hydrophobic tail and a hydrophilic head. It has previously been documented in literature how aqueous surfactant solutions have the tendency to form long flexible cylindrical aggregates, frequently referred to as worm-like micelles (Khatory et al., 1993). This association of surfactants in solution can be explained by considering the critical packing parameter $P_c = v/l_c a_o$, where l_c is the extended chain length, a_o is the interfacial surface area occupied by the headgroup and v is the volume of the headgroup. Depending on this value, various micellar structures are formed in solution such as: spherical, worm-like, vesicles, planar bilayer, inverted micelles, etc (Stuart and Boekema, 2007). If the value of the packing parameter lies in between 1/3 and 1/2, cylindrical wormlike micelles can be expected (Dreiss, 2017; Trickett and Eastoe, 2008). If the concentration of these cylindrical structures in solution is high enough, they are capable of forming entangled networks and subsequently increasing the viscoelastic properties of the aqueous solution (Cates and Candau, 1990). This property has seen application in several areas such as oil, gas, consumer goods, etc (Yang, 2002). The use of cosurfactants or the addition of salt has also been considered to promote the formation of longer cylindrical aggregates, by decreasing the net interfacial surface area (Parker and Fieber, 2013; Trickett and Eastoe, 2008).

Supramolecular chemistry looks at dynamic noncovalent interactions between molecules, which are reversible in nature and thus open the possibility of fine-tuning their architectures and properties (Huang and Scherman, 2012). Some of the interactions that may be taking place between the constituent molecules are: hydrogen bonding, π - π stacking, metal-ligand coordination, hydrophobic interactions, halogen bonding and electrostatic interactions (Barrientos et al., 2019; Huang and Scherman, 2012). Supramolecular networks often have the potential to respond to external stimulants and self-assemble in to interesting architectures which makes them a prime choice for use in design of smart materials (Huang and Scherman, 2012). Not surprisingly, there has been a lot of work in this domain in recent years. Aboudzadeh et al. have designed a novel supramolecular ionic network based on small ionic molecules, particularly citric acid and aliphatic diamines (Aboudzadeh et al., 2012). Yan et al. have demonstrated how certain polymers can utilize hydrogen bonding interactions to form supramolecular gels in the melt phase (Yan et al., 2014).

The use of stimuli to modulate the properties of materials has been an interesting and important area of research. Stimuli-responsive supramolecular networks can be broadly classified as: thermoresponsive (sensitive to temperature), photoresponsive (sensitive to light), chemoresponsive (sensitive to certain chemicals), redox responsive and mechanoresponsive (sensitive to mechanical loading) (Huang and Scherman, 2012). As a specific example, Joung et. al studied a pH-responsive system containing cyclodextrin (Joung et al., 2007). Zhao et al. developed a shear responsive metallo-supramolecular gel which uses metal-ligand interactions (Zhao et al., 2004).

1.3 Scope and Objective of this Thesis

Dynamic binary complexes (DBC) refer to a particular class of supramolecular complexes containing 2 components, whose properties can be changed with a stimulus such as pH, temperature, and salinity. One of the components is usually a long-tailed surfactant or surfactant derivative. The second component is an amine or an acid, depending on the nature of the first component. The stimulus helps form or break the entangled networks in solution. This tunable nature allows us to control and switch the viscosity of an aqueous solution of the DBC. Our group has previously worked on such supramolecular complexes consisting of a long chain amidoamine synthesized with stearic acid complexed with an organic acid (Hao et al., 2018b, 2018a; Yegin et al., 2016). In the previous work, the noncovalent interactions involved were mainly electrostatic bonds between the constituents. This research was taken a step forward in this thesis and other viable dynamic binary complexes were explored, whose unique properties could be attributed to hydrogen bonds. They have the ability to form multi-layered entangled network structures in aqueous solution and thus increase its viscosity. This mechanism is illustrated in Figure 1. The 2 different compounds are held together via hydrogen bonding interactions at high pH. This enables multi-layered aggregates to form in solution. A potential application for these switchable viscous fluids would be in the domain of hydraulic fracturing fluids. For this reason, the potential stimuli has been limited to pH, temperature and salinity and triggers such as CO₂ concentration, redox reactions and light will not be looked into.

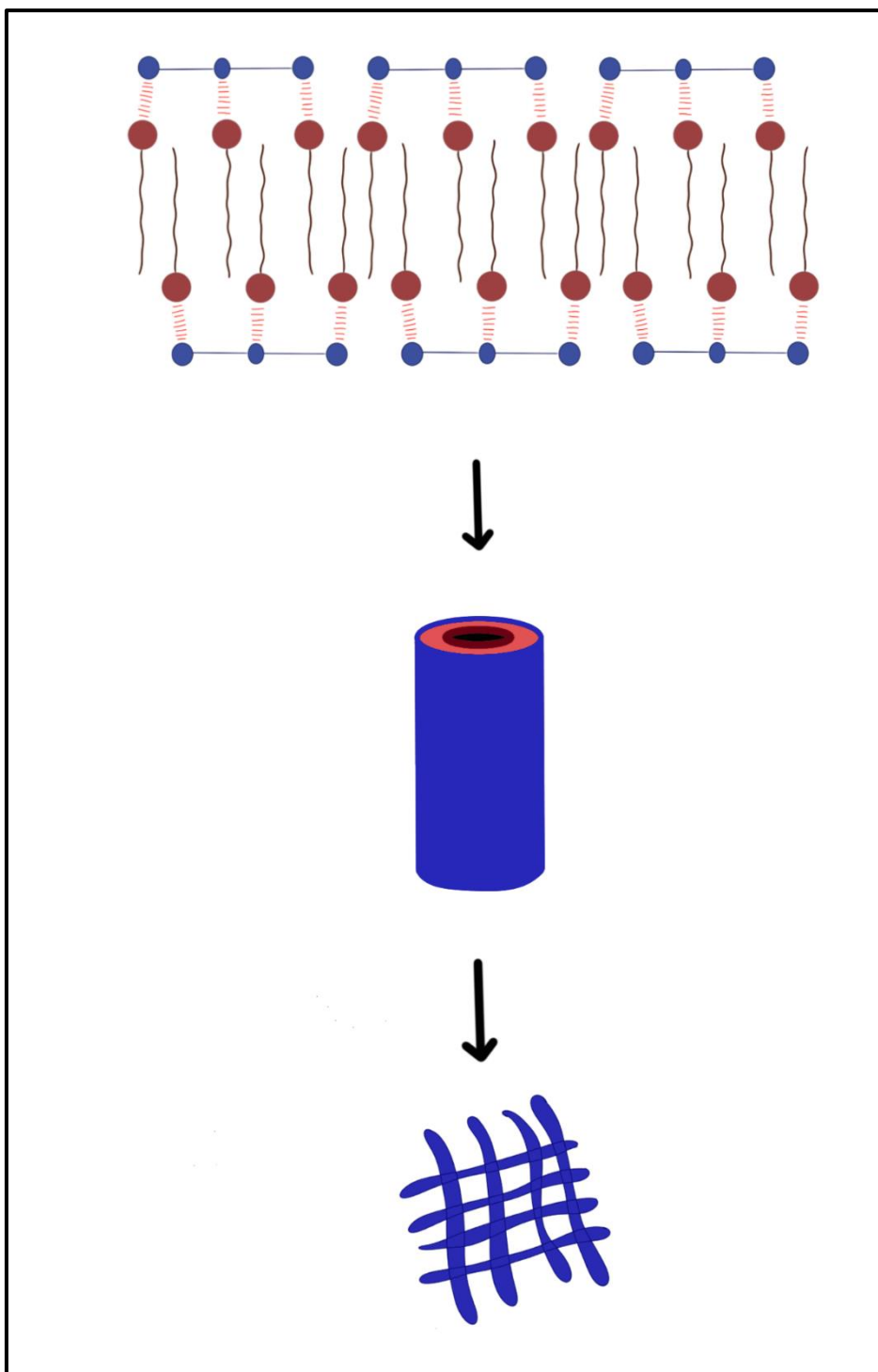


Figure 1: Mechanism of formation of entangled networks in solution by Dynamic Binary Complexes

In this thesis, a novel pH-switchable dynamic binary complex (DBC) will be presented. It is prepared as a simple aqueous solution of oleic acid, which is the major fatty acid present in olive oil along with diethylenetriamine. Figure 2 shows the constituent compounds that make up this system. There are no major synthesis steps involved as the two constituents are held together by non-covalent interactions. This solution can be switched between low-viscosity and high-viscosity regimes by simply changing the pH. This would be useful in the hydraulic fracturing space since it can be kept viscous while carrying the proppant and its viscosity can then be reduced during the flowback stage. Its viscous properties were pronounced upon the addition of salt to the mixture. Rheological characterization of the solution was done as a function of pH and salt concentration. Furthermore, sand settling tests were also performed to assess its proppant carrying capability. The fact that salt enhances its properties is a major advantage since it opens the possibility of using seawater, rather than precious freshwater for preparation of fracturing fluid.

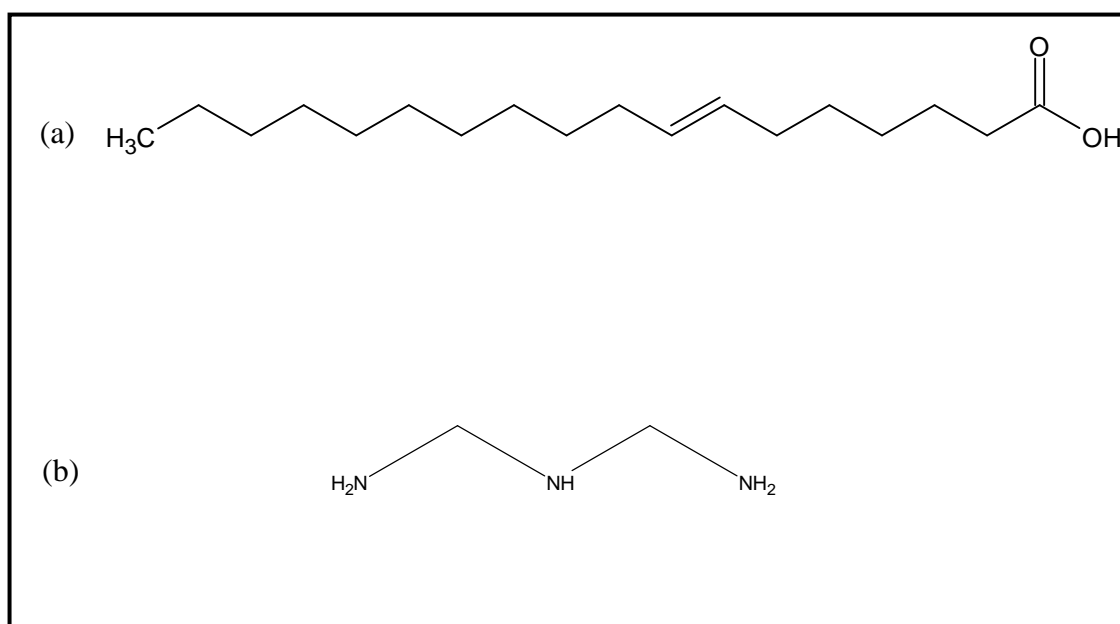


Figure 2: (a) Structure of Oleic Acid, (b): Structure of Diethylenetriamine

2. MATERIALS AND METHODS

2.1 Materials and Sample Preparation

Oleic Acid (>90%, technical grade) was purchased from Alfa Aesar (Ward Hill, MA, USA). Diethylenetriamine (>98%, for synthesis), Sodium Chloride (>99%, ACS Reagent) and Polyacrylamide were purchased from Sigma Aldrich (St. Louis, MO, USA). Colored sand particles were obtained from Ashland Global Speciality Chemicals (Wilmington, DE, USA). The solutions were prepared by mixing oleic acid and diethylenetriamine in distilled water such that the total weight of the two components added up to less than or equal to 2 % weight of the solution. Both 2 wt% and 1 wt% DBC solutions were made. The ratio of the two components was Oleic acid: Diethylenetriamine :: 3:1. Sodium chloride was also stirred in some of the mixtures as 1 wt% or 3 wt% of the total solution. The solution was stirred in a beaker with a magnetic stirrer for ~24 hours.

2.2 Rheological Measurements

Rheology measurements were conducted using a rotational rheometer (Haake RS 1, Thermo Fisher Scientific, Waltham, MA, USA). Parallel plate geometry was used with a 20 mm tip (PP20 Ti) for measurements. The gap between the plate and tip was primarily kept at 1 mm. The shear rate was increased logarithmically and stepwise (15 steps) from 0.001 s^{-1} to 100 s^{-1} and viscosity was measured at each step. Zero frequency viscosities were determined by extrapolating the viscosity versus shear rate curves to near zero values. This rheometer was also used to measure the frequency dependent viscoelastic properties (storage and loss modulus) for frequencies in between 0.01 s^{-1} and 100 s^{-1} . All rheological measurements were taken three times for

statistical analysis. Due to the formation of precipitates below pH 8, the range of operation of this study was kept basic (pH 9-12). The salinity of the solution was also varied. The total weight percentage of the formulation in solution was 1 wt% or 2 wt%. The pH was adjusted by adding 10 wt% H₂SO₄ or 10 wt% NaOH to the DBC solution and was allowed to sit for a day for self-assembly of the solution.

2.4 Sand Settling Test

To gauge how the dynamic binary complex solutions would hold up proppant, sand settling tests were performed. 7 wt% of blue colored sand particles were dispersed and agitated in vials of dynamic binary complex solution of differing pH and salinity. High quality images were taken after the following intervals: 1 min, 10 min, 1 hr, 2 hr, 4 hr, 8 hr and 24 hr to see how much of the dispersed sand settled within that time frame. This experiment was conducted at 23°C and 90°C.

2.5 Microscopy Analysis

In order to see the microstructural changes that take place in the supramolecular solution, images were taken using an optical microscope (Bioryx 200, Arryx Inc, Chicago, IL, USA). Images were captured at pH 9 and pH 11 to understand the solution and micellar assembly behavior that leads to major changes in the rheological properties.

3. RESULTS AND DISCUSSION

3.1 Sensitivity to pH

This particular dynamic binary complex was observed to exhibit extremely viscous gel like behavior at high pH in the presence of NaCl. Both 1 wt% and 2 wt% DBC exhibited this property when the salt concentration was 1 wt% or 3 wt%. However, salt free solutions did not have such pronounced rheological characteristics. Figure 3(a) shows the viscosity trends for 1 wt% DBC + 3 wt% salt. A similar trend was observed even in Figure 3(b), which shows the viscosity variation of 2 wt% DBC + 1 wt% NaCl. Gel like structures and high viscosities were observed in both the cases at pH 11 and 12, despite the lower concentration of DBC in Figure 2(a). Even at higher shear rates of 100 s^{-1} , the viscosity values were in the range of 40-500 cP. The viscosity became significantly lower in both the cases as the pH was decreased to 9 or 10.

This switchable property can be explained by diving deeper in to the nature of interactions between the constituent components of the dynamic binary complex. The pKa of oleic acid is around 9.85. Above this pH, it is completely present in its disassociated form as an anion. Furthermore, as the pH is increased, the diethylenetriamine loses all its extra protons and becomes a neutral molecule. This gives rise to a situation where hydrogen bonding can take place between oleic acid and diethylenetriamine, such that self-assembly of the constituents into long elongated wormlike structures can occur (Zhou et al., 2014). This phenomenon is explained further in section 3.5. This pH tunability gives the option of easy cleanup of the reservoir by simply reducing the pH. This would prevent residue formation in the fissures, which has been a leading cause of concern since it reduces the relative permeability of gas (Tannich, 1975).

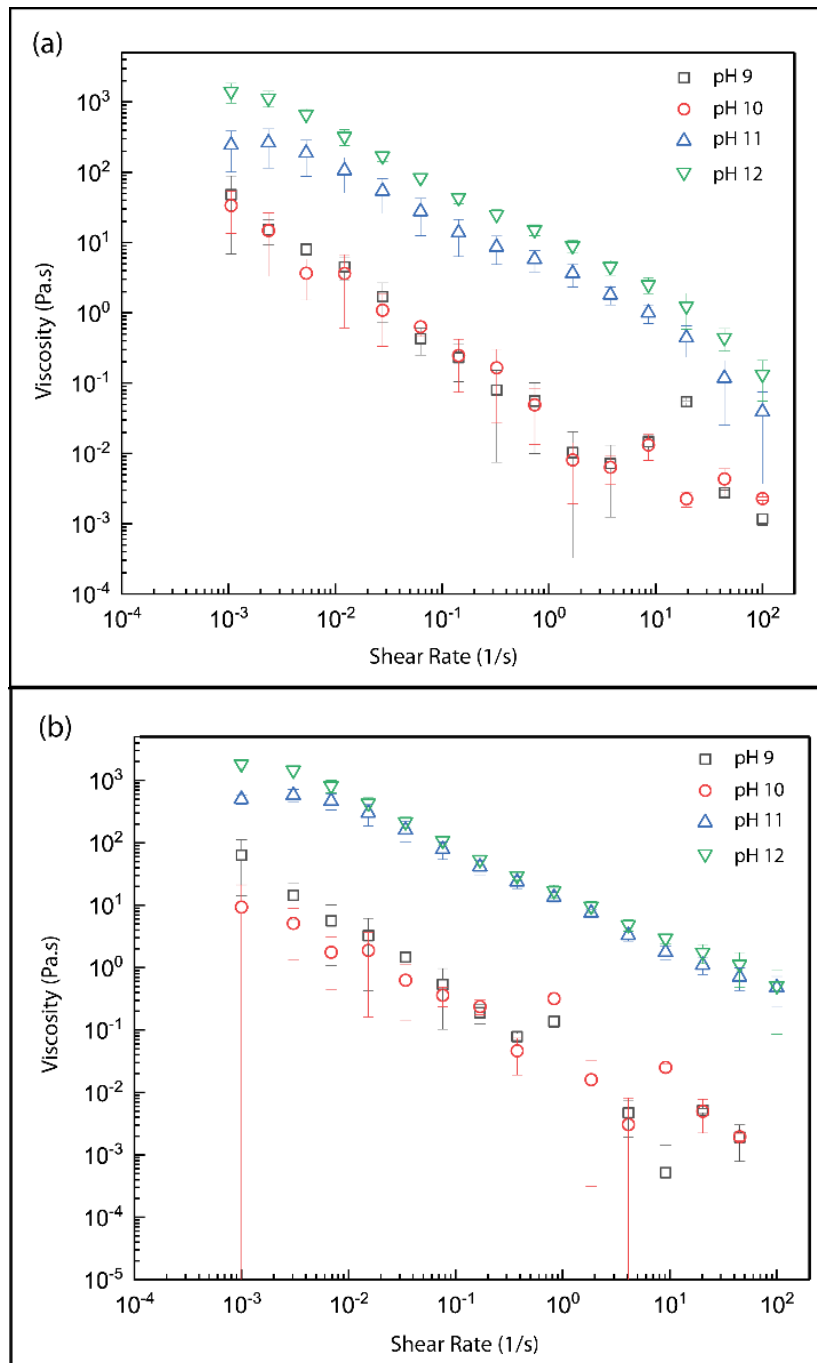


Figure 3: Viscosity variation with pH of (a) 1 wt% DBC solution + 3 wt% NaCl, (b) 2 wt% DBC solution + 1 wt% NaCl. The error bars indicate the standard deviation.

Figure 4 was plotted to quantify the pH switchable property further. Solutions of polyacrylamide (PAM), which is a major component of the commercial fracturing fluid known as slickwater (Palisch et al., 2010) were prepared as a control. Comparison

between 2 wt% DBC, 1 wt% DBC, 1 wt% PAM and 2 wt% PAM was done. All of the solutions contained 3 wt% salt as well to measure performance under salinity. The zero-frequency viscosity was plotted as a function of the pH. It can be seen that the PAM solutions did not exhibit any obvious sensitivity to pH whereas the zero-frequency viscosity of the DBC solution increased by a factor as large as ~280 when pH was increased from 9 to 12. The zero shear viscosity is an important parameter that determines proppant transport (Asadi et al., 2002). Overall, the zero shear viscosities were higher for the DBC solutions as compared to the PAM solutions.

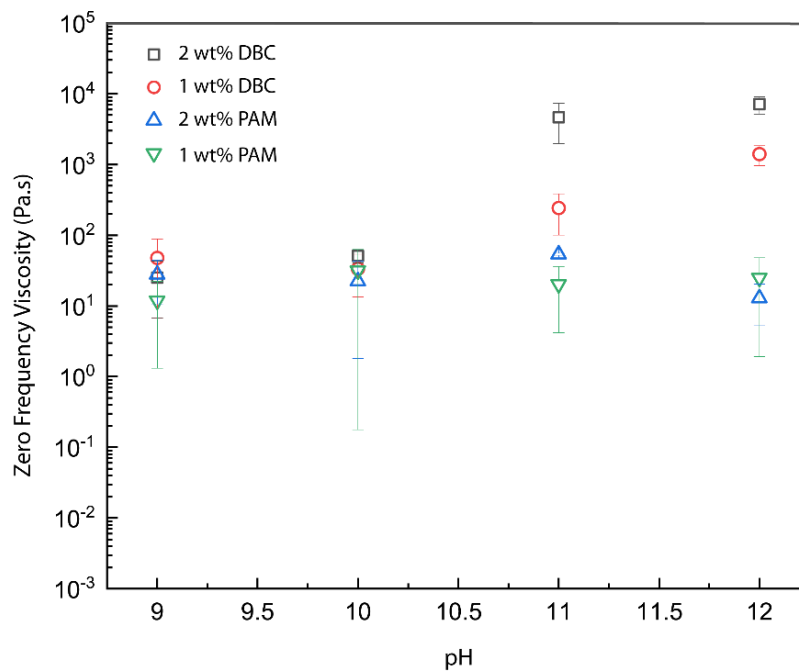


Figure 4: Zero Frequency Viscosity Comparison between 2 wt%, 1 wt% Polyacrylamide(PAM) solution and 2 wt%, 1 wt% Dynamic Binary Complex(DBC) solution. All the solutions contain 3 wt% NaCl. The error bars indicate standard deviation.

3.2 Viscoelastic Test Results

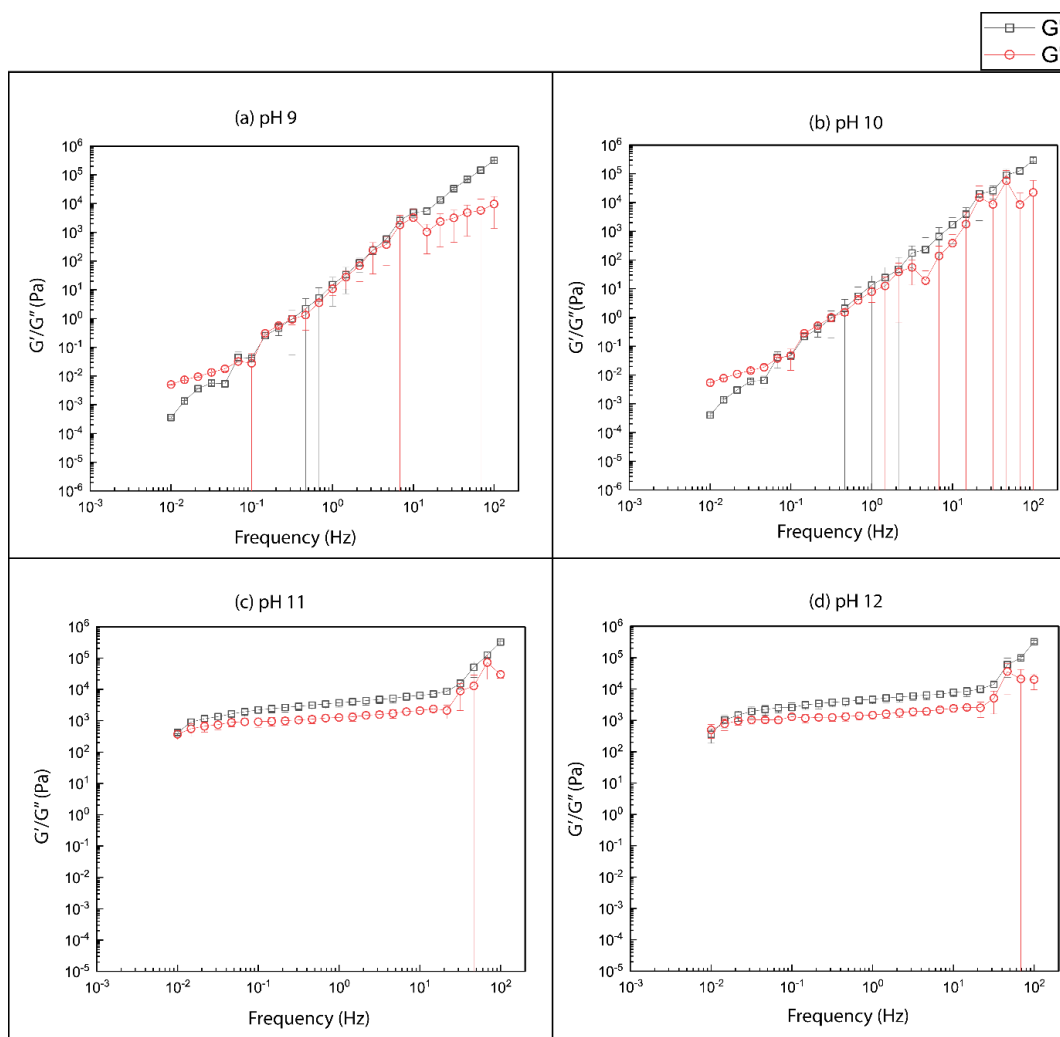


Figure 5: Storage (G') and loss (G'') moduli of 2wt% DBC+3wt% salt at (a)pH 9, (b)pH 10, (c)pH 11, (d)pH 12. The error bars indicate standard deviation

In order to further evaluate the rheological characteristics of the DBC solutions, the storage (G') and loss (G'') moduli were measured in the frequency range 0.01-100 for 2 wt% DBC+3wt% salt solution. The results of this are presented in Figure 5. At pH 9 and 10, both the moduli increased linearly on the log-log plot, indicating exponential increase with critical frequency ~ 0.1 . After this critical frequency, the solution would tend to flow instead of deform. In other words, it enters the region where the proppant

would tend to settle more swiftly (Loveless et al., 2011). For the pH 11/pH 12 case, an extended plateau was observed till a frequency of $\sim 20 \text{ s}^{-1}$. This points towards a highly structured complex fluid, similar to the viscoelastic behavior that has previously been observed in crosslinked polymer based fracturing fluids (Gomaa et al., 2014). Also since $G' > G''$ throughout, the fluid had considerable elasticity which would increase the resistance towards settling of proppant (Gomaa et al., 2015).

3.3 Effect of Salinity

Figure 6 shows the rheological behavior of 2 wt% DBC solution at different salt concentrations. The pH was maintained at 11, where high viscosity was expected for all samples. Interestingly, the overall viscosity increased as the salt concentration was increased. This can be attributed to the fact that the presence of salt screens the electrostatic repulsions such that hydrogen bonding interactions between disassociated oleic acid and neutral diethylenetriamine can dominate (Jean-François Berret, 2006; Zhou et al., 2014).

The use of freshwater for fracturing has been an environmental and sustainability concern for a long time (Gallegos et al., 2016). Most conventional viscoelastic surfactants have the problem of low salt tolerance (X. Yang et al., 2019b) and hence require freshwater for their preparation. Therefore, a formulation such as the one presented in this paper, which can be prepared using salt water from the ocean would prove to be both ecofriendly and economically viable.

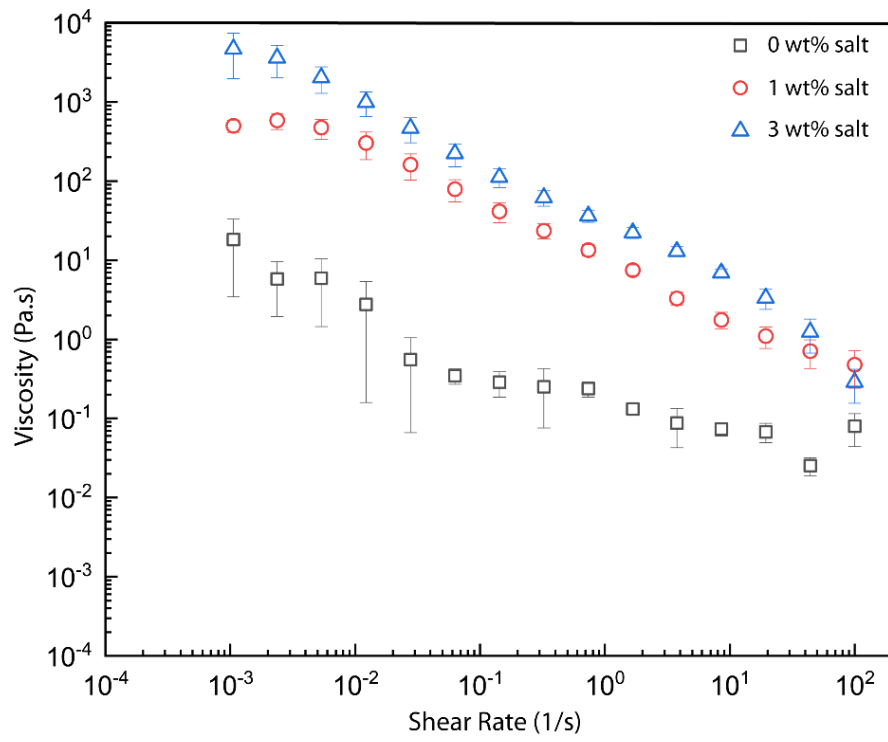


Figure 6 : Effect of Salinity on the Viscosity of 2 wt% DBC at pH 11

3.4 Sand Settling Test

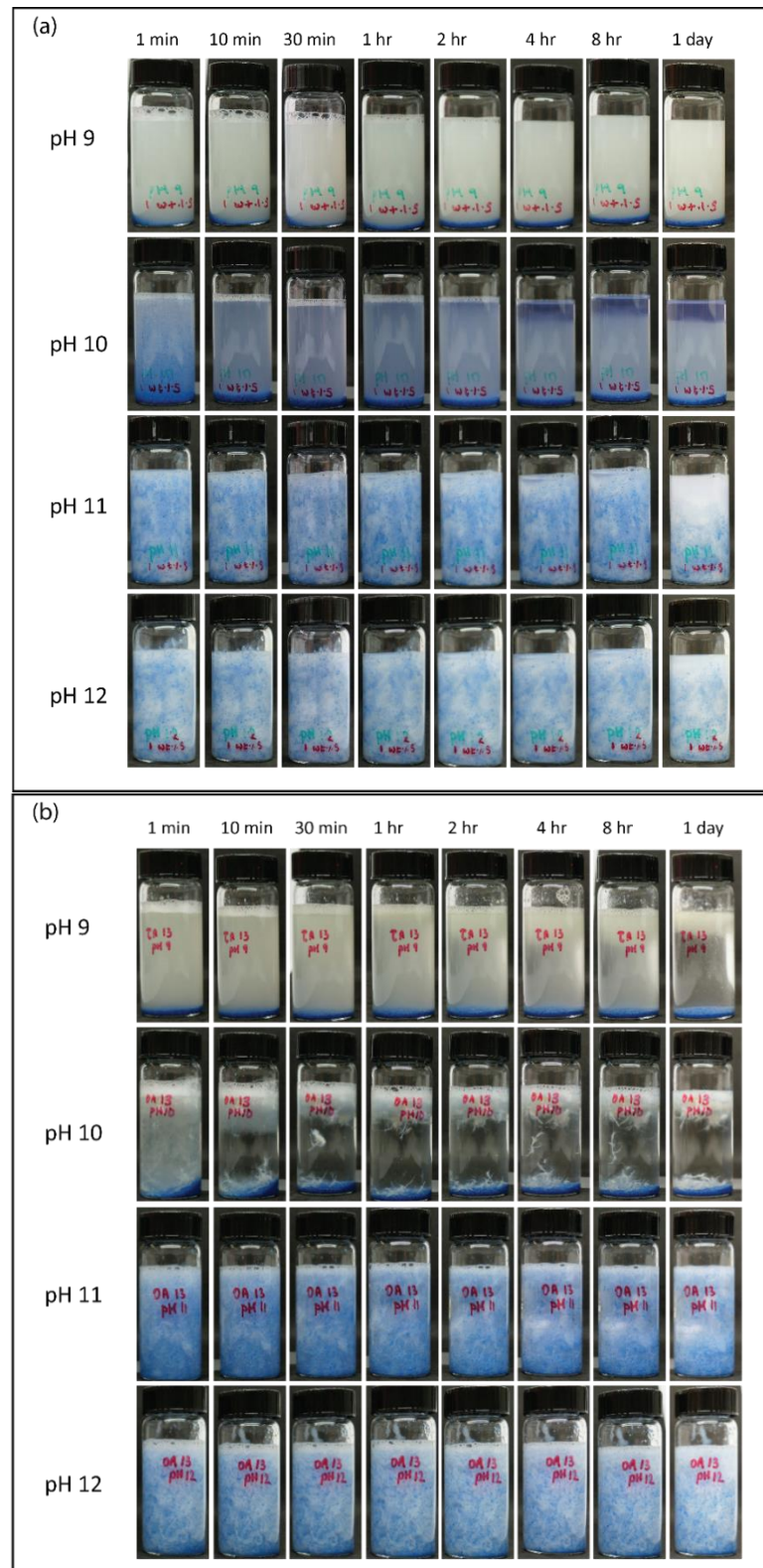


Figure 7: Sand Settling Test for (a) 1 wt% DBC + 1 wt% salt at room temperature (23°C) (b) 1 wt% DBC + 3 wt% salt at room temperature (23°C)

Sand settling test helps give a clear picture of the potential of the DBC as a proppant carrier. The results obtained for both 1 wt% and 2 wt% DBC have been promising. Figure 7 shows images of dispersed sand in DBC solution for 1 wt% DBC+1 wt% salt and 1 wt% DBC+3 wt% salt. Superior sand carrying capability is clearly visible at pH 11 and pH 12 in both cases. Even after 24 hours, the sand stayed dispersed in the matrix and did not settle. This is enough for most hydraulic fracturing applications, which requires sand of varying mesh sizes to be dispersed in the fluid until it settles to the bottom of the fracture (Daneshy, 1978). The contrast in the sand settling times was clearly visible for the DBC at pH 9 and pH 10 since it could not hold sand for even a minute at that pH. Hence, we have visual proof of the pronounced pH-sensitive switchable nature. Furthermore, without the presence of NaCl in the solution, the sand settling times were observed to be in the range of a few seconds, allowing us to conclude that the results are enhanced by salinity.

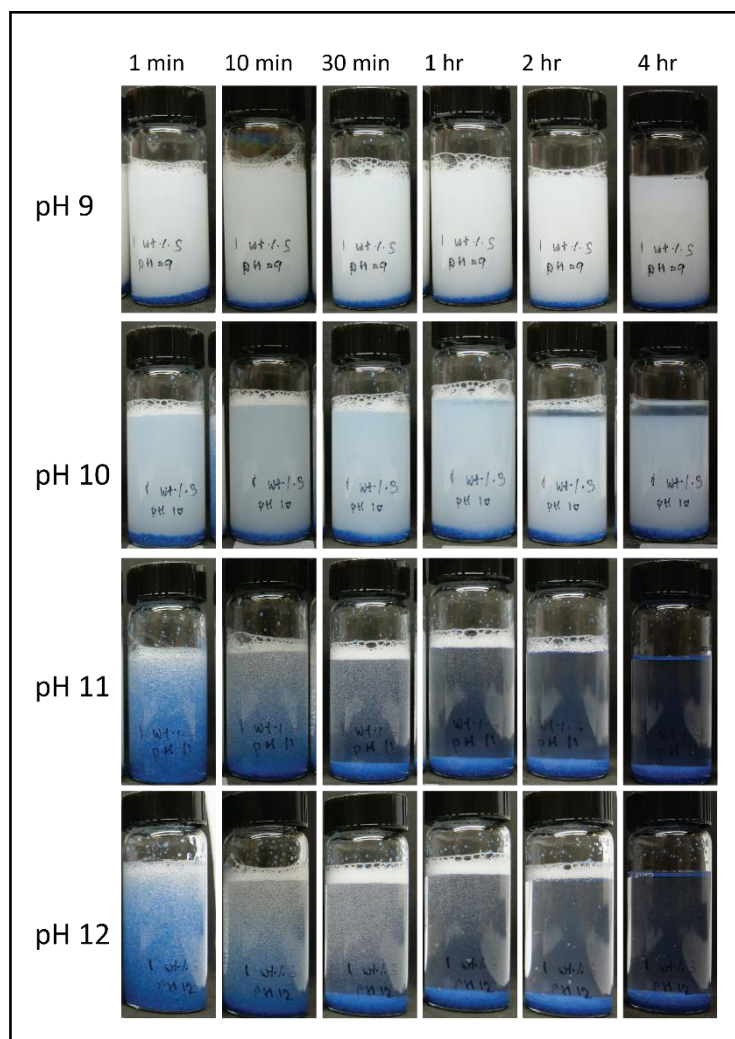


Figure 8 : Sand settling test at 90°C of 2 wt% DBC + 3 wt% salt

In order to assess its application potential in reservoirs, where the fracturing fluid is exposed to higher temperature gradients, especially during the flowback period (S. Yang et al., 2019), the sand settling test was also conducted at an elevated temperature of 90°C. The results for 2 wt% DBC+3 wt% salt are presented in Figure 8. Though the overall sand settling time decreased as compared to the ambient temperature case, a pH-switchable behavior was still observed. The samples at pH 11 and pH 12 had a settling time of around 12 minutes in contrast to almost immediate settling at pH 9 and pH 10. The decreased viscosities at this temperature along with the pH tunability could prove to be beneficial during flowback of fluid.

3.5 Microscopy Results and Microstructure

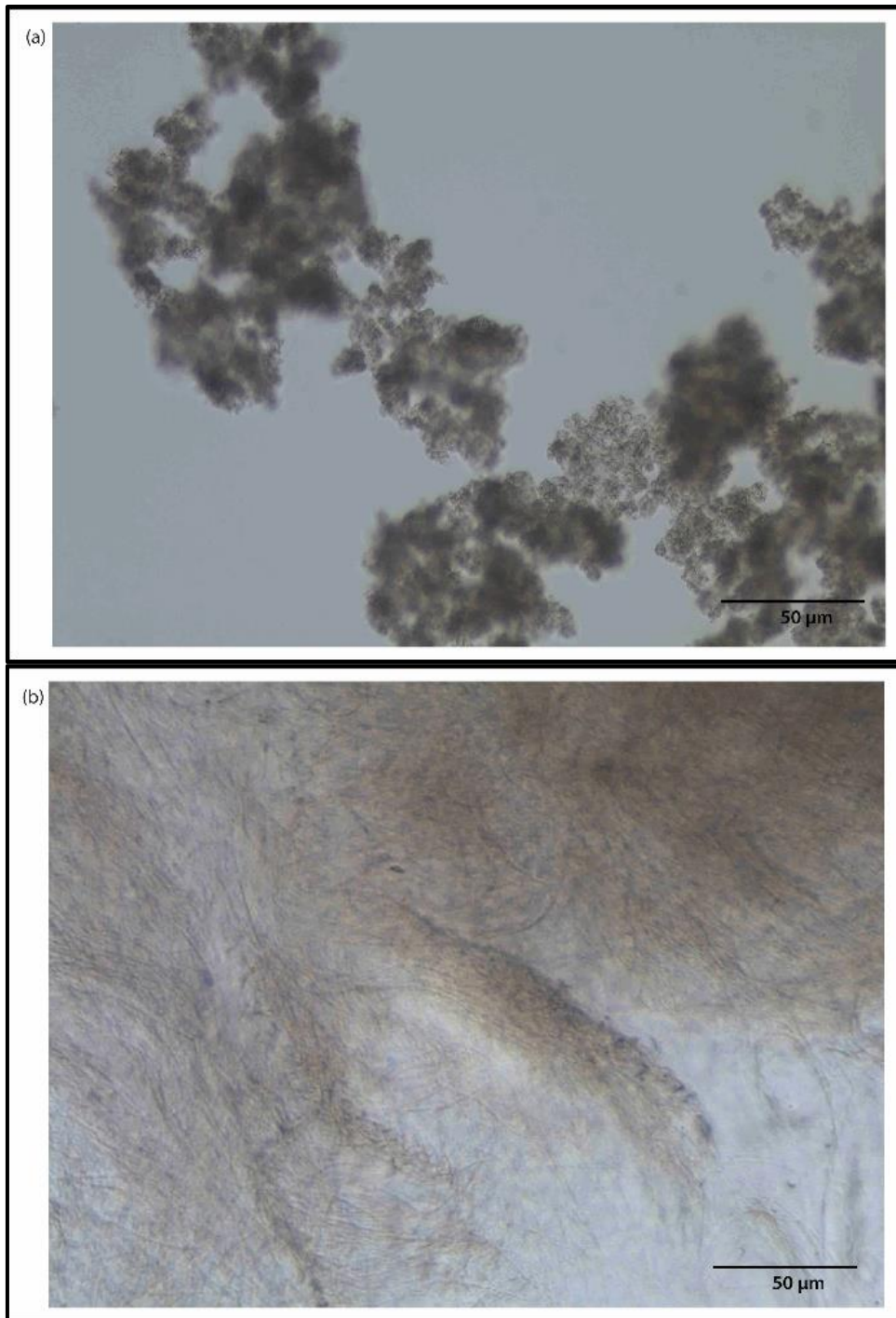


Figure 9: Optical microscopy images (30x magnification) of 2 wt% DBC + 3 wt% NaCl solutions at (a) pH 9 and (b) pH 11

With the intention of visually inspecting the microstructure that gives rise to the viscous gel like behavior, optical microscopy was done at pH 9 and 11 as shown in figure 9. An entangled network of fibrous structures was seen in the micrograph for pH 11 whereas circular structures were observed at pH 9. It has previously been reported in literature that in the pH range of 8-10, this system forms giant vesicles in solution and forms a more network-like structure as the pH is increased even more (Zhou et al., 2014). It can even be considered that as the pH increases, the packing parameter of the binary system decreases towards 0.5 due to an increase in interfacial surface area, favoring elongated structure formation (Dreiss, 2017; Trickett and Eastoe, 2008). This may be taking place as the nature of interactions is moving from the electrostatic regime into the hydrogen bonding regime. It is quite conceivable that self-assembly of the constituents into the network like structure is what contributes to the large viscosity values and gel formation and subsequently its ability to hold up sand particles. A previous study that highlighted the relationship between proppant suspension behavior and microstructure also alludes towards the importance of fibrillar network structure of a gel in its ability to hold up proppant (Wang et al., 2014).

3.6 Application Potential

During the process of hydraulic fracturing, it is desirable to have an initially high viscosity during proppant transport. After the fluid injection step is completed and the proppant is deposited in the fractures, the fracturing fluid must attain a lower viscosity to allow flow back and efficient cleanup (Jennings Jr, 1996). The use of oxidizers and enzymes have sometimes been utilized for this purpose in linear and crosslinked gels, but their incompatibility towards certain fracturing fluids and additives prompted the search for alternatives (Fuller, 2016; Gunawan et al., 2012). The dynamic binary complex presented in this paper, which can be switched down to a lower viscosity by decreasing the pH has the potential to address the gel breaking requirements of industry in a facile manner. Commercially, borate cross-linked fracturing fluids are widely used pH switchable aqueous fracturing fluids (Kruijf et al., 1993; Norman et al., 1995). However, they have been reported to have poor stability in the presence of seawater (Kruijf et al., 1993). Our dynamic binary complex system poses the additional advantage of working under saline conditions.

Traditional viscoelastic surfactants usually utilize external conditions in the reservoir such as contact with hydrocarbons or brine in order to break the gel and reduce the viscosity (Crews et al., 1990; Huang and Crews, 2008; Zhang et al., 2018). However, there are disadvantages associated with this, especially in dry reservoirs, and it has been noticed that relying on external conditions to break the fluid often creates the need for remedial cleanup (Huang and Crews, 2009, 2008). The utilization of an acid as a breaker, as proposed in this paper would have the potential to deliver more consistent results since the addition of acid can be controlled by the operator. It is also possible to consider the use of biodegradable acids like citric acid to fulfill this purpose, increasing the ecological viability of the process.

4. FUTURE WORK

Apart from the system discussed here, several other systems with the potential to form dynamic binary complexes can be explored. It may be useful to consider different long chain compounds or different complexing agents. Zhu et al. has reviewed surfactant systems with properties similar to that of gemini surfactants that are bound together by noncovalent interactions (Zhu et al., 2016). Also, it is important to further understand the factors that may contribute to increase in temperature and salt tolerance of these complexes.

4.1 Different Long-Chain Compounds

Amidosulfobetaines are a class of surfactant compounds that have shown wormlike micellar properties, thus giving rise to viscoelastic solutions (Chu et al., 2010; Chu and Feng, 2010). They can be formed via a 2-step synthesis mechanism as shown in Figure 10, with stearic acid as the starting compound. Direct amidation of stearic acid using N,N'-Dimethyl-1,3-propanediamine followed by quaternization of the product by 1,3-Propanesultone are the key steps in this process (Chu and Feng, 2009). These synthesized surfactants can then be used to form dynamic binary complexes by complexation with diethylenetriamine, to see whether tunable properties are observed.

Another compound with an interesting structure that has the potential to be used in this manner can be N-Oleoylsarcosine. It has previously been used in the petroleum industry as a rust inhibitor (Pines and Spivack, 1956). It can also be complexed with diethylenetriamine to attempt to form dynamic binary complexes.

Gemini surfactants are a class of surfactants with multiple hydrophilic heads and tails, that have shown potential in the field of enhanced oil recovery and hydraulic fracturing

as well (Kamal, 2016; Zhang et al., 2018). Akbas et al. have presented a facile way of synthesizing a cationic gemini surfactant by using an amidoamine and 1,10-dibromodecane (Akbaş et al., 2016). Also, Pal. et al have demonstrated a way by which non-ionic gemini surfactants can be synthesized by the use of sunflower oil (Pal et al., 2019). It would be interesting to explore ways by which these compounds could be incorporated as a constituent of a DBC

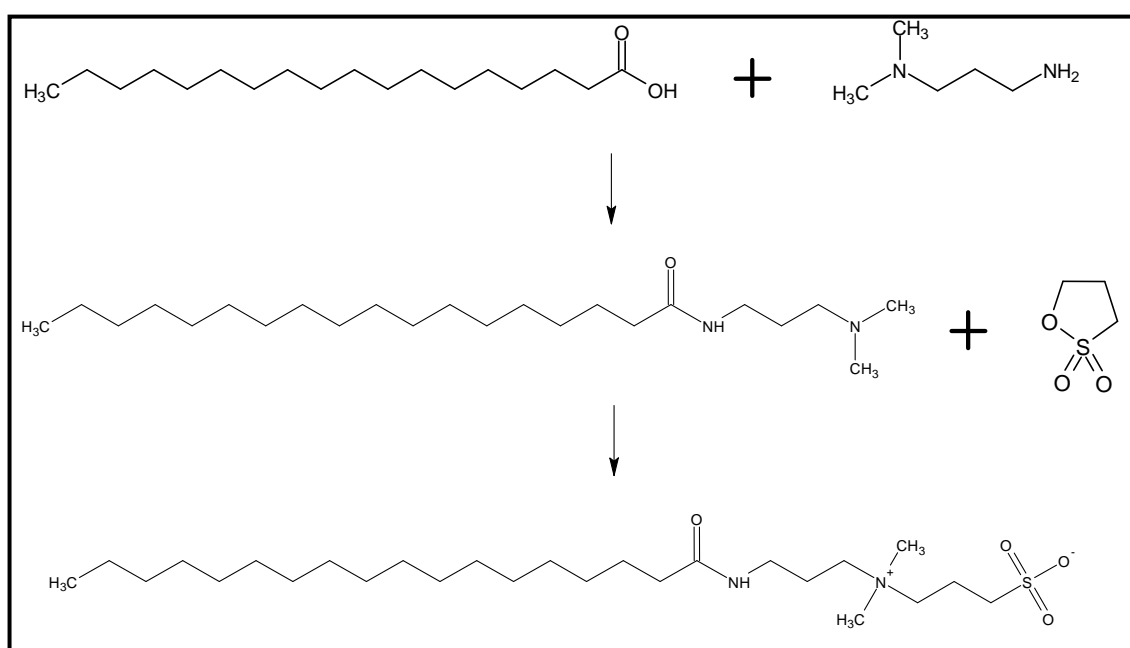


Figure 10: Mechanism for synthesis of amidosulfobetaine compounds

4.2 Different Complexing Agents

Apart from diethylenetriamine, different complexing agents may be considered for oleic acid. Amines such as N,N,N',N'-Tetramethylethylenediamine or N,N'-Dimethyl-1,3-propanediamine may be considered for this purpose.

If a surfactant that is cationic or a non-ionic surfactant that becomes positive upon changing the pH is being used, amines are not a suitable complexing agent. In this case, it becomes useful to consider organic acids as previously demonstrated by our group in the case of amidoamine complexed with malic acid/ citric acid. Kang et. al have seen pH-responsive wormlike formation upon complexing a type of amidoamine with isomers of phthalic acid (Kang et al., 2018). In a similar fashion, Wang et. al have studied pH-responsive wormlike systems consisting of CTAB and phthalic acid (P. Wang et al., 2019). Therefore, phthalic acid may be considered as a complexing agent for future work.

5. CONCLUSION

This thesis presents a novel dynamic binary complex (DBC), based on supramolecular networks whose viscous and viscoelastic properties are highly sensitive to pH and salinity. The preparation of the solution did not require any complex synthesis and simply involved stirring together oleic acid and diethylenetriamine in the appropriate ratio (3:1). DBC solutions of both 2 wt% and 1 wt% were prepared and both of them exhibited a gel-like behavior under saline conditions at a pH of 11 and above. Their viscosity could be brought down by decreasing the pH, thus making them pH tunable solutions. Viscoelastic tests suggested a complex fluid structure favorable for holding proppant. Additionally, sand settling tests of these solutions exhibited their potential to hold particles for a long period, for example, over 24 hours. Even at elevated temperatures, they could hold the proppant for several minutes. Optical micrographs showed the differences in self-assembled structures at pH 9 and pH 11 which were responsible for the divergent rheological properties. This simple formulation has the potential to be used as a hydraulic fracturing fluid whose viscosity can be tuned with pH, with the potential to improve proppant transport. An additional advantage lies in its potential to be prepared with seawater, rather than freshwater due to its efficacy in saline conditions. Further work would include experimenting with different types of constituent compounds such that their viscoelastic properties improve and they are able to exhibit increased tolerance towards high temperature.

REFERENCES

- Abdul Majid, A.B., Hansen, J.E., Al-Dahlan, M.N., Malik, A.R., Alharbi, M.M., Al-Suwaigh, M.K., Atwi, M.A., Shammari, N.S., Alkhaldi, M.H., Abel, J.T., Alsalman, M.A., 2017. Seawater based fracturing fluid: A game changer in hydraulic fracturing applications in Saudi Arabia. *SPE Middle East Oil Gas Show Conf. MEOS, Proc.* 2017-March, 2445–2459. <https://doi.org/10.2118/184015-ms>
- Aboudzadeh, M.A., Muñoz, M.E., Santamaría, A., Fernández-Berridi, M.J., Irusta, L., Mecerreyes, D., 2012. Synthesis and rheological behavior of supramolecular ionic networks based on citric acid and aliphatic diamines. *Macromolecules* 45, 7599–7606. <https://doi.org/10.1021/ma300966m>
- Akbaş, H., Kocaoğlu, S., Boz, M., Dikmen, A., 2016. A novel cationic Gemini surfactant with amide group: synthesis and micellization behavior in aqueous solutions. *Colloid Polym. Sci.* 294, 1439–1451. <https://doi.org/10.1007/s00396-016-3905-8>
- Al-Muntasheri, G.A., Liang, F., Hull, K.L., 2017. Nanoparticle-enhanced hydraulic-fracturing fluids: A review. *SPE Prod. Oper.* 32, 186–195. <https://doi.org/10.2118/185161-PA>
- Asadi, M., Conway, M.W., Barree, R.D., Viscosity, Z.S., 2002. An Essential Parameter In Proppant Transport Characterizations. *SPE Int. Symp. Exhib. Form. Damage Control SPE 73755*, 1–10.
- Barrientos, L., Miranda-Rojas, S., Mendizabal, F., 2019. Noncovalent interactions in inorganic supramolecular chemistry based in heavy metals. Quantum chemistry point of view. *Int. J. Quantum Chem.* 119, 1–16. <https://doi.org/10.1002/qua.25675>
- Blauch, M.E., 2010. Developing effective and environmentally suitable fracturing fluids using hydraulic fracturing flowback waters. *SPE Unconv. Gas Conf.* 2010 257–268. <https://doi.org/10.2523/131784-ms>
- Castro Dantas, T.N., Santanna, V.C., Dantas Neto, A.A., Alencar Moura, M.C.P., 2005. Hydraulic gel fracturing. *J. Dispers. Sci. Technol.* 26, 1–4. <https://doi.org/10.1081/DIS-200040161>
- Cates, M.E., Candau, S.J., 1990. Statics and dynamics of worm-like surfactant micelles. *J. Phys. Condens. Matter* 2, 6869–6892.
- Chen, J., Al-Wadei, M.H., Kennedy, R.C.M., Terry, P.D., 2014. Hydraulic fracturing: Paving the way for a sustainable future? *J. Environ. Public Health* 2014. <https://doi.org/10.1155/2014/656824>
- Chu, Z., Feng, Y., 2010. Amidosulfobetaine surfactant gels with shear banding transitions. *Soft Matter* 6, 6065–6067. <https://doi.org/10.1039/c0sm00874e>
- Chu, Z., Feng, Y., 2009. A facile route towards the preparation of ultra-long-Chain amidosulfobetaine surfactants. *Synlett* 2655–2658. <https://doi.org/10.1055/s-0029-1217973>
- Chu, Z., Feng, Y., Su, X., Han, Y., 2010. Wormlike micelles and solution properties of

- a C22-tailed amidosulfobetaine surfactant. *Langmuir* 26, 7783–7791.
<https://doi.org/10.1021/la904582w>
- Crews, J.B., Huang, T., Tools, B.O., 1990. SPE 106216 Internal Breakers for Viscoelastic - Surfactant Fracturing Fluids 1–8.
- Daneshy, A.A., 1978. Numerical Solution of Sand Transport in Hydraulic Fracturing. *JPT, J. Pet. Technol.* 30, 132–140. <https://doi.org/10.2118/5636-PA>
- Dreiss, C.A., 2017. Wormlike Micelles: An Introduction. *RSC Soft Matter* 2017-Janua, 1–8. <https://doi.org/10.1039/9781782629788-00001>
- Fuller, M.J., 2016. An innovative approach to gel breakers for hydraulic fracturing. *SPE Int. Form. Damage Control Symp. Proc.* 2016-Janua, 24–26. <https://doi.org/10.2118/178991-ms>
- Gallegos, T.J., Varela, B.A., Haines, S.S., Engle, M.A., 2016. Hydraulic fracturing water use variability in the United States and potential environmental implications. *Water Resour. Res.* 6621–6642. <https://doi.org/10.1002/2015WR017278>.Received
- Gomaa, A.M., Gupta, D.V.S., Carman, P., 2015. Proppant Transport? Viscosity Is Not All It's Cracked Up To Be 2–5.
- Gomaa, A.M., Gupta, D.V.S., Carman, P., 2014. Viscoelastic behavior and proppant transport properties of a new associative polymer-based fracturing fluid. *SPE - Eur. Form. Damage Conf. Proceedings, EFDC* 1, 1–17. <https://doi.org/10.2118/168113-ms>
- Gunawan, S., Armstrong, C.D., Qu, Q., 2012. Universal breakers with broad polymer specificity for use in alkaline, high-temperature fracturing fluids. *Proc. - SPE Annu. Tech. Conf. Exhib.* 3, 2201–2209. <https://doi.org/10.2118/159396-ms>
- Hasan, A.M.A., Abdel-Raouf, M.E., 2018. Applications of guar gum and its derivatives in petroleum industry: A review. *Egypt. J. Pet.* 27, 1043–1050. <https://doi.org/10.1016/j.ejpe.2018.03.005>
- Hoffmann, H., 2003. Viscoelastic Surfactant Solutions 2–31. <https://doi.org/10.1201/9780203911518.ch10>
- Hu, Y.T., Chung, H.C., Maxey, J., 2015. What is more important for proppant transport, viscosity or elasticity? *Soc. Pet. Eng. - SPE Hydraul. Fract. Technol. Conf.* 2015 206–216. <https://doi.org/10.2118/173339-ms>
- Huang, F., Scherman, O.A., 2012. Supramolecular polymers. *Chem. Soc. Rev.* 41, 5879–5880. <https://doi.org/10.1039/c2cs90071h>
- Huang, T., Crews, J.B., 2009. Fluid-loss control improves performance of viscoelastic surfactant fluids. *SPE Prod. Oper.* 24, 60–65. <https://doi.org/10.2118/106227-pa>
- Huang, T., Crews, J.B., 2008. Do viscoelastic-surfactant diverting fluids for acid treatments need internal breakers? *Proc. - SPE Int. Symp. Form. Damage Control* 2, 855–862.
- Hull, K.L., Sayed, M., 2016. Recent Advances in Viscoelastic Surfactants for Improved Production From Hydrocarbon Reservoirs.

- Jasechko, S., Perrone, D., 2017. Hydraulic fracturing near domestic groundwater wells. *Proc. Natl. Acad. Sci. U. S. A.* 114, 13138–13143.
<https://doi.org/10.1073/pnas.1701682114>
- Jean-François Berret, 2006. Chapter 19 RHEOLOGY OF WORMLIKE MICELLES : EQUILIBRIUM PROPERTIES AND SHEAR. *Rheology* 667–720.
- Jennings Jr, A.R., 1996. *Fracturing Fluids-Then and Now*.
- Jiang, Q., Jiang, G., Wang, C., Zhu, Q., Yang, L., Wang, L., Zhang, X., Liu, C., 2016. A new high-temperature shear-tolerant supramolecular viscoelastic fracturing fluid. *Soc. Pet. Eng. - IADC/SPE Asia Pacific Drill. Technol. Conf.* 1–11.
<https://doi.org/10.2118/180595-MS>
- Kamal, M.S., 2016. A Review of Gemini Surfactants: Potential Application in Enhanced Oil Recovery. *J. Surfactants Deterg.* 19, 223–236.
<https://doi.org/10.1007/s11743-015-1776-5>
- Kang, W., Zhao, Y., Wang, P., Li, Z., Hou, X., Huang, Z., Yang, H., 2018. Rheological behavior and mechanism of pH-responsive wormlike micelle variations induced by isomers of phthalic acid. *Soft Matter* 14, 4445–4452.
<https://doi.org/10.1039/c8sm00467f>
- Khatory, A., Lequeux, F., Kern, F., Candau, S.J., 1993. Linear and Nonlinear Viscoelasticity of Semidilute Solutions of Wormlike Micelles at High Salt Content. *Langmuir* 9, 1456–1464. <https://doi.org/10.1021/la00030a005>
- Kruijf, A.S., Roodhart, L.P., Davies, D.R., 1993. Relation between chemistry and flow mechanics of borate-crosslinked fracturing fluids. *SPE Prod. Facil.* 8, 165–169.
<https://doi.org/10.2118/25206-pa>
- Loveless, D., Holtsclaw, J., Saini, R., Harris, P., Fleming, J., 2011. Fracturing fluid comprised of components sourced solely from the food industry provides superior proppant transport. *Proc. - SPE Annu. Tech. Conf. Exhib.* 5, 3775–3782.
<https://doi.org/10.2118/147206-ms>
- Miller, R.G., Sorrell, S.R., 2004. The future of oil supply. *Int. J. Veh. Des.* 35, 9–26.
<https://doi.org/10.1504/ijvd.2004.004363>
- Norman, L., Vitthal, S., Terracina, J., 1995. New breaker technology for fracturing high-permeability formations. *SPE - Eur. Form. Damage Conf. Proceedings, EFDC 1995-May*, 187–199. <https://doi.org/10.2523/30097-ms>
- Owen, N.A., Inderwildi, O.R., King, D.A., 2010. The status of conventional world oil reserves-Hype or cause for concern? *Energy Policy* 38, 4743–4749.
<https://doi.org/10.1016/j.enpol.2010.02.026>
- Pal, N., Samanta, K., Mandal, A., 2019. A novel family of non-ionic gemini surfactants derived from sunflower oil: Synthesis, characterization and physicochemical evaluation. *J. Mol. Liq.* 275, 638–653.
<https://doi.org/10.1016/j.molliq.2018.11.111>
- Palisch, T.T., Vincent, M.C., Handren, P.J., 2010. Slickwater fracturing - Food for thought. *Soc. Pet. Eng. - SPE Asia Pacific Oil Gas Conf. Exhib. 2010, APOGCE 2010 1*, 24–43.

- Parker, A., Fieber, W., 2013. Viscoelasticity of anionic wormlike micelles: Effects of ionic strength and small hydrophobic molecules. *Soft Matter* 9, 1203–1213. <https://doi.org/10.1039/c2sm27078a>
- Pines, R.M., Spivack, J.D., 1956. A laboratory study of N-oleoyl sarcosine as a rust inhibitor in some petroleum products. *Preprints* 1, 289–294.
- Siddhamshetty, P., Kwon, J.S. II, Liu, S., Valkó, P.P., 2018. Feedback control of proppant bank heights during hydraulic fracturing for enhanced productivity in shale formations. *AIChE J.* 64, 1638–1650. <https://doi.org/10.1002/aic.16031>
- Siddhamshetty, P., Mao, S., Wu, K., Kwon, J.S.-I., 2020. Multi-Size Proppant Pumping Schedule of Hydraulic Fracturing: Application to a MP-PIC Model of Unconventional Reservoir for Enhanced Gas Production. *Processes*. <https://doi.org/10.3390/pr8050570>
- Stuart, M.C.A., Boekema, E.J., 2007. Two distinct mechanisms of vesicle-to-micelle and micelle-to-vesicle transition are mediated by the packing parameter of phospholipid-detergent systems. *Biochim. Biophys. Acta - Biomembr.* 1768, 2681–2689. <https://doi.org/10.1016/j.bbamem.2007.06.024>
- Tannich, J.D., 1975. Liquid Removal From Hydraulically Fractured Gas Wells. *JPT, J. Pet. Technol.* 27, 1309–1317. <https://doi.org/10.2118/5113-PA>
- Trickett, K., Eastoe, J., 2008. Surfactant-based gels. *Adv. Colloid Interface Sci.* 144, 66–74. <https://doi.org/10.1016/j.cis.2008.08.009>
- Wang, J., Zhou, F., Bai, H., Li, Y., Yang, H., 2020. A Comprehensive method to evaluate the viscous slickwater as fracturing fluids for hydraulic fracturing applications. *J. Pet. Sci. Eng.* 193, 107359. <https://doi.org/10.1016/j.petrol.2020.107359>
- Wang, P., Zhu, T., Hou, X., Zhao, Y., Zhang, X., Wang, T., Yang, H., Kang, W., 2019. Responsive wormlike micelle with pH-induced transition of hydrotrope based on dynamic covalent bond. *J. Mol. Liq.* 286. <https://doi.org/10.1016/j.molliq.2019.110935>
- Wang, S., Chen, F., Guo, J., Li, Y., Zhao, F., Zhou, S.Y., 2019. Adsorption damage of hydroxypropyl guar gum to porous media composed of quartz. *J. Pet. Sci. Eng.* 182, 106379. <https://doi.org/10.1016/j.petrol.2019.106379>
- Wang, S., Zhang, Y., Guo, J., Lai, J., Wang, D., He, L., Qin, Y., 2014. A study of relation between suspension behavior and microstructure and viscoelastic property of guar gum fracturing fluid. *J. Pet. Sci. Eng.* 124, 432–435. <https://doi.org/10.1016/j.petrol.2014.09.016>
- Wang, Z., Krupnick, A., 2015. A retrospective review of shale gas development in the United States: What led to the boom? *Econ. Energy Environ. Policy* 4, 5–17. <https://doi.org/10.5547/2160-5890.4.1.zwan>
- Wanniarachchi, W.A.M., Ranjith, P.G., Perera, M.S.A., 2017. Shale gas fracturing using foam-based fracturing fluid: a review. *Environ. Earth Sci.* 76, 1–15. <https://doi.org/10.1007/s12665-017-6399-x>
- Whitlock, L., Sanders, A., Knox, P., 2015. The evaluation of polycationic, carbohydrate-based surfactants as viscoelastic (VES) fracturing fluids. *Proc. - SPE*

- Int. Symp. Oilf. Chem. 2, 1155–1167. <https://doi.org/10.2118/173791-ms>
- Yan, T., Schröter, K., Herbst, F., Binder, W.H., Thurn-Albrecht, T., 2014. Nanostructure and rheology of hydrogen-bonding telechelic polymers in the melt: From micellar liquids and solids to supramolecular gels. *Macromolecules* 47, 2122–2130. <https://doi.org/10.1021/ma402007f>
- Yang, J., 2002. Viscoelastic wormlike micelles and their applications. *Curr. Opin. Colloid Interface Sci.* 7, 276–281. [https://doi.org/10.1016/S1359-0294\(02\)00071-7](https://doi.org/10.1016/S1359-0294(02)00071-7)
- Yang, J., Cui, W., Guan, B., Lu, Y., Qiu, X., Yang, Z., Qin, W., 2016. Supramolecular fluid of associative polymer and viscoelastic surfactant for hydraulic fracturing. *SPE Prod. Oper.* 31, 318–324. <https://doi.org/10.2118/175762-PA>
- Yang, S., Lai, F., Li, Z., Fu, Y., Wang, K., Zhang, L., Liang, Y., 2019. The effect of temperature on flowback data analysis in shale gas reservoirs: A simulation-based study. *Energies* 12, 1–23. <https://doi.org/10.3390/en12193751>
- Yang, X., Mao, J., Chen, Z., Chen, Y., Zhao, J., 2019a. Clean fracturing fluids for tight reservoirs: opportunities with viscoelastic surfactant. *Energy Sources, Part A Recover. Util. Environ. Eff.* 41, 1446–1459. <https://doi.org/10.1080/15567036.2018.1548520>
- Yang, X., Mao, J., Chen, Z., Chen, Y., Zhao, J., 2019b. Clean fracturing fluids for tight reservoirs: opportunities with viscoelastic surfactant. *Energy Sources, Part A Recover. Util. Environ. Eff.* 41, 1446–1459. <https://doi.org/10.1080/15567036.2018.1548520>
- Yegin, C., Zhang, M., Talari, J.V., Akbulut, M., 2016. Novel hydraulic fracturing fluids with improved proppant carrying capacity and pH-adjustable proppant deposition behavior. *J. Pet. Sci. Eng.* 145, 600–608. <https://doi.org/10.1016/j.petrol.2016.06.033>
- Yekeen, N., Padmanabhan, E., Idris, A.K., 2018. A review of recent advances in foam-based fracturing fluid application in unconventional reservoirs. *J. Ind. Eng. Chem.* 66, 45–71. <https://doi.org/10.1016/j.jiec.2018.05.039>
- Yekeen, N., Padmanabhan, E., Idris, A.K., Chauhan, P.S., 2019. Nanoparticles applications for hydraulic fracturing of unconventional reservoirs: A comprehensive review of recent advances and prospects. *J. Pet. Sci. Eng.* 178, 41–73. <https://doi.org/10.1016/j.petrol.2019.02.067>
- Zhang, W., Mao, J., Yang, X., Zhang, H., Zhang, Z., Yang, B., Zhang, Y., Zhao, J., 2018. Study of a novel gemini viscoelastic surfactant with high performance in clean fracturing fluid application. *Polymers (Basel)*. 10. <https://doi.org/10.3390/polym10111215>
- Zhao, Y., Beck, J.B., Rowan, S.J., Jamieson, A.M., 2004. Rheological behavior of shear-responsive metallo-supramolecular gels. *Macromolecules* 37, 3529–3531. <https://doi.org/10.1021/ma0497005>

- Zhou, C., Cheng, X., Zhao, O., Liu, S., Liu, C., Wang, J., Huang, J., 2014. The evolution of self-assemblies in the mixed system of oleic acid-diethylenetriamine based on the transformation of electrostatic interactions and hydrogen bonds. *Soft Matter* 10, 8023–8030. <https://doi.org/10.1039/c4sm01204f>
- Zhu, L., Tang, Y., Wang, Y., 2016. Constructing Surfactant Systems with the Characteristics of Gemini and Oligomeric Surfactants Through Noncovalent Interaction. *J. Surfactants Deterg.* 19, 237–247. <https://doi.org/10.1007/s11743-016-1790-2>