

ENCAPSULATION OF SURFACTANTS INTO SILICA NANOSIZED
PARTICLES: MECHANISIM OF CONTROLLED RELEASE, LIQUID-
SOLID AND LIQUID-LIQUID INTERACTIONS FOR ENHANCED
OIL RECOVERY APPLICATIONS

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ABSTRACT

Removal or recovery of oil, which is either attached to a solid surface or as an emulsion in water is an ongoing challenge. Its removal and recovery could be challenging due to the strong interactions of the polar groups of oil to the charged solid surfaces. Moreover, large surface tension forces result in low mobility of the oil emulsions. To that end, surfactants could be utilized to mobilize oil. However, excess of surfactant molecules could hinder their effectiveness due to the formation of micelles or bilayers. Additionally, adsorption of surfactant molecules to the rock-solid surfaces leads to having surfactant unnecessarily wasted and results in higher costs.

In this thesis, a new controlled surfactant delivery system via encapsulation of cationic and anionic surfactants into mesoporous silica nanoparticles will be described. Encapsulation of the cationic surfactant resulted in hexagonal mesoporous particles of around 50 nm in diameter. The anionic surfactant encapsulation resulted in hollow-spherical like nanoparticles.

The responsive and controlled release of the surfactant molecules from the mesoporous particles was studied in simulated high salinity and high temperature conditions that are normally encountered in subsurface environment. The surfactant molecules were released from the nanosized porous particles in response to the ions present in solution and high temperature (conditions typically encountered in a reservoir).

The ability of the suspension in mobilizing oil attached to a solid surface was studied via sessile drop contact angle measurements. We concluded that the release of the surfactants transforms an oil-wet surface to water-wet due to the favorable partitioning

of the surfactants at the interface. Moreover, the improved interfacial properties of the nanoparticles were assessed by dynamic interfacial tension at the oil-water interface. The performance of the new system resulted in decreasing the interfacial tension up to three orders of magnitude. This reduction outweighs the performance of the bare surfactant or neat nanoparticles.

BIOGRAPHICAL SKETCH

Ahmed holds a Bachelor's degree in Chemical Engineering from King Fahd University of Petroleum and Minerals and is currently a Master's student in Giannelis group at Cornell University, where his research is focused toward encapsulating surfactants into silica nanoparticles for the slow release of the surfactants for improving the interfacial properties of oil-water mixtures. Prior to joining Cornell University, Ahmed worked at Saudi ARAMCO for three years, where his interest in nanotechnology for oil and gas application arose. Ahmed's experience in Saudi ARAMCO ranges from working in the EXPEC Advanced Research Centre (EXPEC ARC) to working as a reservoir engineer for Khurais Increment project and finally as a production engineer in the CO₂-EOR Pilot project.

To my mother and father, Ghadeer and Wesam

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TABLE OF CONTENTS

CHAPTER 1 INTRODUCTION AND OVERVIEW	1
1.1 Energy Outlook and Enhanced Oil Recovery	1
1.2 Encapsulation for EOR and Mesoporous Silica Nanoparticles	6
1.3 Overcoming the Forces: Liquid-Solid and Liquid-Liquid Interactions.....	9
1.3.1 Liquid-Solid Interaction: Wettability	9
1.3.2 Liquid-Liquid Interaction: Interfacial Tension.....	10
REFERENCES	11
CHAPTER 2 SLOW RELEASE OF SURFACTANT UTILIZING SILICA NANOSIZED CAPSULES	16
Abstract.....	16
2.1 Introduction	17
2.2 Experimental Section.....	21
2.2.1 Materials	21
2.2.2 Synthesis.....	21
2.2.3 Methods	22
2.3 Results and Discussion	23
2.3.1 Characterization.....	23
2.3.2 Release Experiments	27
Conclusion.....	35
Acknowledgments	36
REFERENCES	37
CHAPTER 3 RESPONSIVE NANOSIZED CAPSULES FOR ACHIEVING ULTRALOW INTERFACIAL TENSION AND WETTABILITY ALTERATION ..	41
Abstract.....	41
3.1 Introduction	42
3.2 Experimental Section.....	45
3.2.1 Materials	45
3.2.2 Synthesis.....	46
3.2.3 Apparatus and Methods.....	46
3.3 Results and Discussion	47
3.3.1 Characterization.....	47
3.3.2 Wettability Alteration	50
3.3.2.1 Wettability Alteration of Silica Surface	50
3.3.2.2 Wettability Alteration of Carbonate Surfaces	54
3.3.3 Responsive System.....	57
3.3.4 Interfacial tension study	58
Conclusion.....	65
Acknowledgment.....	65
REFERENCES	67
CHAPTER 4 ENCAPSULATION OF ANIONIC SURFACTANTS: SIZE CONTROL, SLOW RELEASE AND POTENTIAL USE FOR ENHANCED OIL RECOVERY APPLICATIONS	73
Abstract.....	73

4.1 Introduction	74
4.2 Experimental Section.....	76
4.2.1 Materials	76
4.2.2 Synthesis of DOWFAX Capsules	77
4.2.3 Characterization.....	77
4.2.4 Release Experiments	78
4.2.5 Wettability Alteration Experiments.....	78
4.2.6 Interfacial Tension Measurements	79
4.3 Results and Discussion.....	79
4.3.1 Optimization of the Nanocapsules Size.....	79
4.3.2 Slow Release of DOWFAX.....	82
4.3.3 Wettability Alteration Performance	84
4.3.4 Interfacial Tension Experiment	91
Conclusions	95
Acknowledgment.....	95
REFERENCES	96
Supporting Information	101

CHAPTER 1

INTRODUCTION AND OVERVIEW

1.1 Energy Outlook and Enhanced Oil Recovery

The majority of world energy production is based primarily on fossil fuels. According to Sheng,¹ more than 85% of the world energy consumed is produced from fossil fuels. Moreover, based on British Petroleum 2019 statistical review, oil remains the most used fuel in the energy mix as shown in **Fig. 1**. Furthermore, energy demand is projected to increase by 30% by 2030.

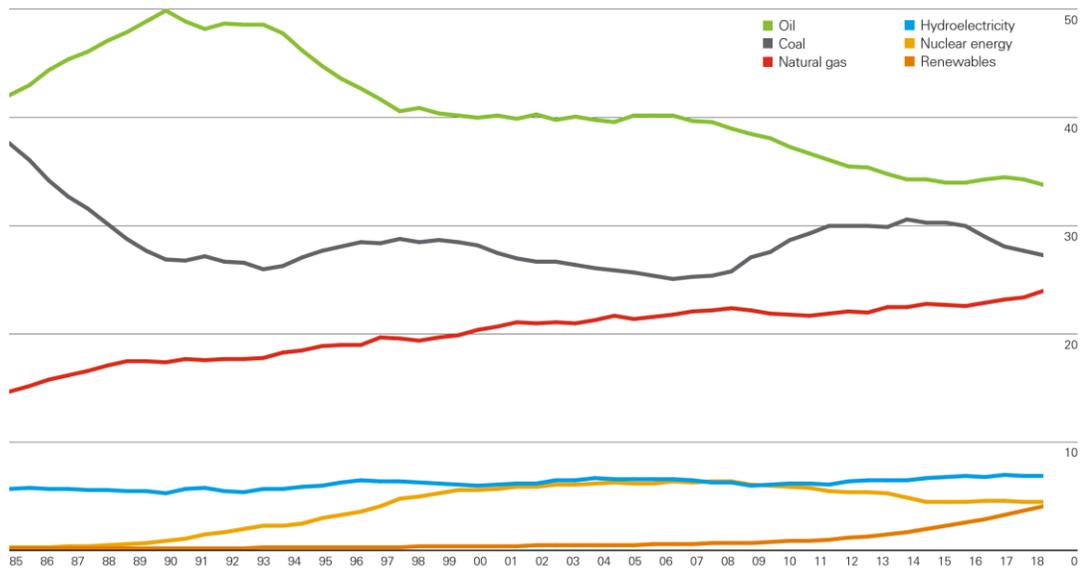


Figure 1: Shares of global energy consumption by the type of fuel where oil remains to be at the front of the energy supply (BP,2019 statistical review)

In order to meet this energy demand, more hydrocarbon reserves and increased levels of production are needed. Carbonate reservoirs hold more than 60% of the oil and 40% of the gas reservoirs. The proven oil reserves, which is the oil that is producible with today's technology, is estimated to be 1,730 billion barrels as indicated in **Fig. 2**.

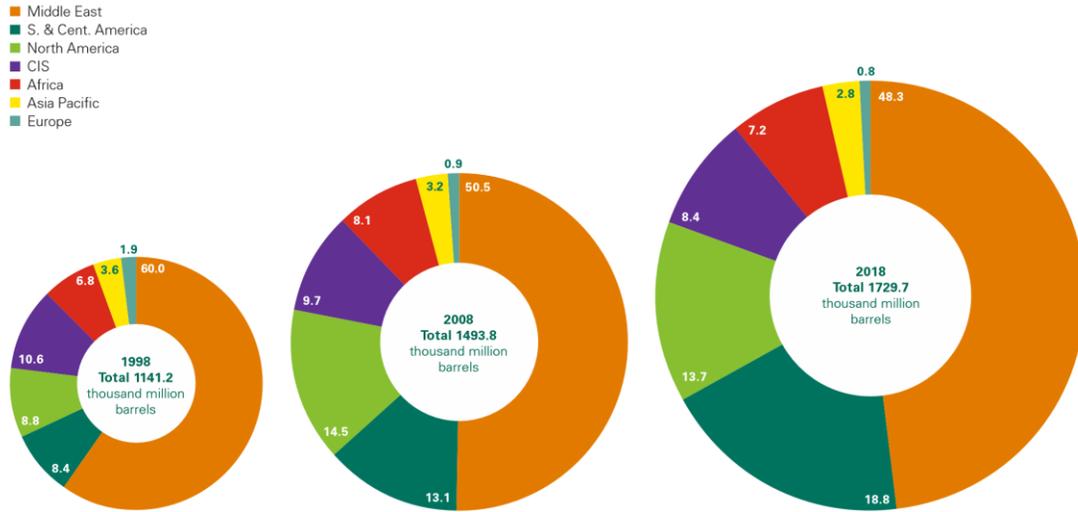


Figure 2: Proved oil reserves in 1998, 2008 and 2018 (BP, 2019 statistical review)

However, the recovery factor due to physical and chemical limitations could be as low as 35%. With this, there is more than 80 years of oil production leaving more than 50% unproduced. Currently, most of the oil production is through the injection of seawater of varying salinities. However, seawater alone cannot overcome the forces that hinder increased production. Hence, efficient technologies are needed to enhance the oil recovery.¹⁻³

The oil recovery efficiency is governed by macroscopic (volumetric) and microscopic displacement efficiencies. It is determined by the following equation:

$$E_{ro} = \frac{N_p}{N} \quad 1$$

where N_p is the cumulative oil produced, and N is the original oil in place.

Also, the recovery efficiency could be written as follows:

$$E_{ro} = E_{vo} E_{do} \quad 2$$

Where E_{vo} and E_{do} are the volumetric and microscopic efficiencies, respectfully.

Microscopic displacement E_{do} refers to the displacement of oil at the pore scale. It is the one that can be improved by the injection of chemicals to displace oil.

Its value is estimated by:

$$E_{do} = \frac{S_{oi} - S_{or}}{S_{oi}} \quad 3$$

where S_{oi} and S_{or} are the initial and residual oil saturation, respectfully.⁴ As seen from equation 3, to improve the overall oil displacement, the microscopic displacement efficiency needs to increase. Only the residual oil saturation could be manipulated so that the difference between S_{oi} and S_{or} is minimized. Several studies have suggested different methods by which the residual oil saturation is reduced, such as implementing chemicals and nanofluids.^{3,4}

Various Enhanced Oil Recovery (EOR) techniques have been explored including but not limited to the thermal method,^{5,6} gas injection such as CO₂,^{7,8} and chemical (polymer and surfactant) flooding. Among these methods, chemical enhanced oil recovery (cEOR) is one of the most promising and widely used techniques for depleted reservoirs. In particular, surfactant injection has received great attention as a result of its potential to alter the forces that hinder oil production.^{9,10} For instance, it has been reported for different classes of surfactants (ionic and/or nonionic) that they can alter the wettability and reduce the interfacial tension.¹¹⁻¹⁴ Surfactants play a role in altering the wettability of the surface as a result of their adsorption to the reservoir rock. For example, Austad et al. studied wettability alteration of chalk utilizing cationic surfactants. As a result of electrostatic forces, the

carboxylic end of crude oil interacts with the cationic monomer forming an ion-pair, which facilitates desorption from the rock. The proposed mechanism is shown schematically in **Fig. 3**.¹⁵

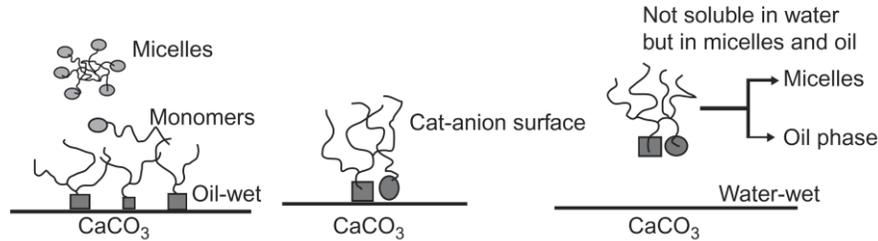


Figure 3: Mechanism of wettability alteration.¹⁵

Anionic surfactants have also been reported to alter the wettability due to their adsorption to positively charged surfaces or the defects that exist between oil film and the solid surfaces.^{1,16}

Nanotechnology has received increased interest more recently for oil applications. Silica nanoparticles, specifically, have been subjected to extensive experimentation for EOR.⁴ One advantage that nanoparticles offer is their large surface area and the ability to functionalize their surfaces chemically, which enhances their surface activity. Another reason is that their size is less than the pore throat size. Hence, they could diffuse into the pores without influencing the permeability. Nanoparticles can increase oil recovery by different mechanisms. They could reduce the interfacial tension, improve viscosity, or change fluid-rock interaction and alter the wettability.¹⁷

There are three areas, where nanotechnology is used for EOR. The first one is nanocatalysis, employed mainly for heavy oil reservoirs, where the nanosized particles facilitate the breakage of carbon-sulfur bonds and hence improve the recovery of the steam injection process.¹⁸ The second type is nanoemulsion, where nanoparticles stabilize emulsions to help manage the mobility ratio (fluid permeability to the viscosity of the injected fluid to the displaced fluid). Nanoemulsions can diffuse into the small pores to displace the trapped oil.¹⁹ The third type is nanofluids, which are basically a stable nanoparticle suspension. The main mechanism by which the nanofluid can enhance oil recovery is by creating a structural disjoining pressure as they assemble like a wedge in the interface of the immiscible phases (solid-liquid).²⁰

While adsorption of surfactants is essential for wettability alteration and partitioning in the oil-water interface is essential to achieve low interfacial tension. High adsorption results in inefficiency in many applications.^{21,22} Adsorption by the rock limits the deep reach of the surfactant in the reservoir where it is anticipated that most of the remaining oil exist. To overcome this challenge, researchers proposed employing synergy between nanotechnology and surfactants to lower the adsorption. For instance, Ahmadi et al. reported the use of hydrophobic nanosilica suspended in a solution containing surfactant, which resulted in lowering the adsorption of surfactant from 14mg/g_{rock} to 4mg/g_{rock} on sandstone rock surface.²³ Similarly, Zargartalebi et al. reported that nanosilica particles reduced the adsorption of anionic surfactants by one order of magnitude.²⁴ However, the surfactants can be physically adsorbed on the surface of the particles, which exposes them to the harsh conditions such as high salinity and temperature, lowering their activity and stability over time. Also, the

surfactant molecules can form bilayers on the surface of the particles, which hinders their adsorption at the oil-water interface. An alternative approach is required in order to develop a more efficient surfactant system.

1.2 Encapsulation for EOR and Mesoporous Silica Nanoparticles

Encapsulation of active molecules into compatible shells for targeting drug delivery has been extensively explored for biomedical applications.^{25,26} More recently, researchers in the oil and gas industry have started exploring this concept for hydrocarbon reservoirs applications. For example, Cortes et al. reported the fabrication of nanocapsules of two types of surfactants and they claimed an efficient reduction of IFT with an increase of the oil recovery by 23%.²⁷ Moreover, Rosestolato and co-workers utilized beeswax as a lipid structure carrying nonylphenol ethoxylate surfactant and studied its performance for EOR applications by means of IFT and wettability alteration.²⁸ However, the previous studies did not propose the mechanism by which the surfactant is released in the bulk fluid. Also, no previous quantification of the amount of surfactant released was provided nor highlighted the relationship between the released amount and the physical phenomenon observed. Most importantly, the physical adsorption of the surfactant to the surface or onto the carriers makes them susceptible to losses in comparison with chemically attached surfactants in the pores of nanoparticles. To overcome this limitation, the concept of engineering nanosized porous material that could release surfactant molecules in response to subsurface stimuli is an attractive concept for EOR applications.

Mesoporous materials represent a flexible platform that could be utilized to encapsulate surfactants. Since their discovery, mesoporous materials have attracted

widespread interest in many applications such as drug delivery and biosensing,²⁹⁻³⁰ water treatment,^{32,33} catalysis^{34,35} and protective coatings.³⁶ Among mesoporous materials, silica-based are promising due to their stability and versatility. What makes silicate mesoporous materials special in comparison to zeolites is the possibility of using long-chain surfactant molecules as structure-directing agents for their synthesis, which is attractive for EOR applications. Moreover, the size of the pore of zeolite is smaller, normally less than 2 nm, where the size of the pore of silicate mesopores could be tailored by the synthesis conditions including the type of surfactants used.

Surfactants are used typically to aid templating of the mesoporous structure. Templating is the process by which the organic molecule plays the central role in structuring the oxide moieties into a crystalline lattice. One type of template is an organic molecule where the inorganic material nucleates and grows around it. For example, the formation of the one material from the silicate mesoporous material now well-known Mobil Composition of Matter No (MCM-41), is suggested to follow a liquid crystal templating mechanism. The cationic surfactant molecules form micelles with the silicate condensing around the surfactant micelles, preserving a hexagonal array. The formation of the mesophases is facilitated by the interactions of the organic and inorganic molecules. In case of ionic surfactants, S^+ or S^- interacts with the inorganic species I^+ or I^- by Coulombic attractions. It is this strong electrostatic interaction that would lead to the formation of a matrix with well-defined pores after removal of the surfactant molecules from the pores. The process is shown in **Fig. 4**.³⁷

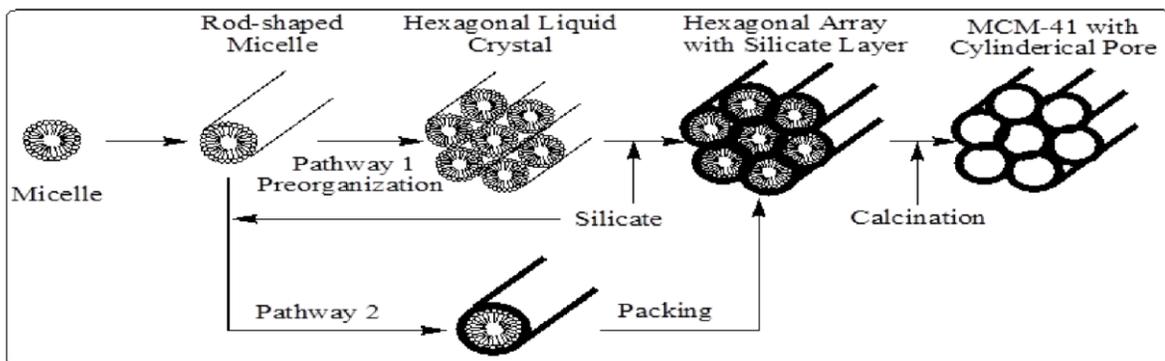


Figure 4: The LCT mechanism for the formation of hexagonal MCM-41.³⁷

Despite their widespread use, mesoporous materials have not been heavily investigated for hydrocarbon recovery applications. One exception is the work of De Freitas et al.³⁸ who proposed utilizing a class of mesoporous materials (SBA-15) to control the delivery of surfactant. They utilized a nonionic surfactant that binds to the surface of the particles and slowly desorbs into the oil-water to lower the interfacial tension of the oil-water interface. However, in their study, the surfactant was physically adsorbed onto the particle surface, which due to the weak interaction between the surfactant and the silica surface can dissociate easily and suffer from the same issues as the neat surfactant injected directly into the reservoir.

In this work, a scalable and facile fabrication of nanosized capsules for the controlled and slow-release of cationic and anionic surfactants is described and its applicability for EOR applications is demonstrated. The system is based broadly on the self-assembly of surfactants in an inorganic material. The material utilized for controlling the release of the cationic surfactants, cetyltrimethylammonium bromide (CTAB), is the well-known MCM-41 described earlier. In contrast, silica hollow spherical capsules are obtained from encapsulating the anionic surfactant

(DOWFAX[®]). The nanosized materials release their cargo in response to the ions in oil field water as a result of the ion exchange mechanism. Moreover, high temperatures further increase the diffusion of surfactant from the mesopores to the bulk fluid. To demonstrate the applicability of the new platform for EOR application, we further investigate the mechanism of altering surface wettability and the reduction of the oil-water interfacial tension.

1.3 Overcoming the Forces: Liquid-Solid and Liquid-Liquid Interactions

1.3.1 Liquid-Solid Interaction: Wettability

“The relative adhesion of two fluids to a solid surface” defines wettability according to Donaldson and Alam.³⁹ More specifically for porous media, it is the tendency for one fluid to wet the surface in the presence of another immiscible fluid. There are essentially four types of wettability: a) water-wet systems in which the rock is covered with a film of water and water is the continuous phase; b) mixed-wet systems, where water occupies the small pores and oil coats the large pores; c) fractionally-wet system where the distribution of wettability is heterogenous throughout the porous medium; and d) oil-wet system where oil exists in the small pores and preferentially coats the larger pores. In oil-wet systems, water does not imbibe spontaneously into the oil-wet rock. Surfaces with a contact angle above 90° are considered oil-wet while those below 90° are water-wet as shown in **Fig. 5**.³⁹ Molecular interactions determine the changes in wettability, which is affected mainly by electrostatic forces between molecules.^{40,41} As stated previously, surfactants are capable of altering the wettability, hence enabling the nonwetting fluid to enter the pores and displace the wetting medium.

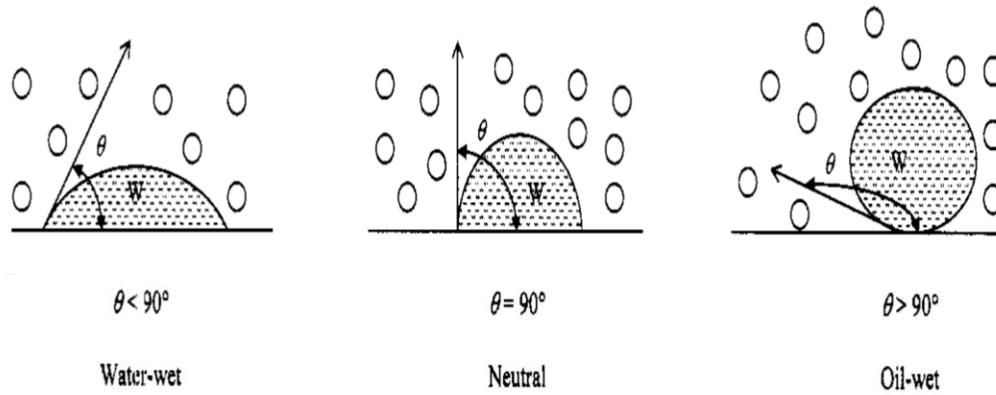


Figure 5: Status of surface wettability according to Donaldson et al. ³⁹

1.3.2 Liquid-Liquid Interaction: Interfacial Tension

The surface free energy that exists at the interface of two immiscible fluids is the surface tension or surface free energy. At the interface, there is a force that attempts to minimize the surface by making it into a sphere. High interfacial tension promotes trapping effects in the porous media which causes a significant decrease in permeability.⁴² In order to increase the oil recovery by improving the microscopic displacement efficiency, the capillary number must be increased.^{43,44} The capillary number is given by the following equation:

$$N_c = \frac{\mu v}{\sigma_{ow}} \quad 4$$

where N_c is the capillary number, μ and v are the viscosity and velocity of the displacing fluid, respectively and σ_{ow} is the oil-water interfacial tension. As indicated by the equation, two possible ways can increase the capillary number: a) increasing the viscosity or b) lowering the interfacial tension. Reducing the interfacial tension by adding surfactants could result in overcoming the capillary forces, which hinder oil production, thereby, improving the oil recovery.⁴⁴

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CHAPTER 2
SLOW RELEASE OF SURFACTANT UTILIZING SILICA NANOSIZED
CAPSULES

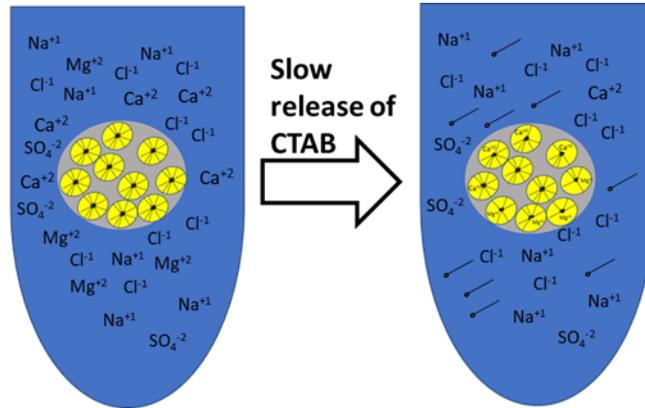
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Abstract

Engineering and scaling-up nanocarriers for the controlled release of surfactant are imperative for enhanced oil recovery (EOR). Herein, the use of silica-based nano-sized porous capsules to slowly release surfactant in saline water is reported. The results indicate that the silica shell ensures the stability of the protected surfactants in the cores under harsh conditions. Almost negligible release was noticed at salt-free brine (DI water). In saline brine, the particles slowly released surfactants molecules. 46% of the total surfactant encapsulated was released after 12 days as quantified by the remaining organic content after mixing with brine. Scanning Electron Microscopy (SEM) analysis confirms the stability of the surfactant incorporated particles in saline water that contains 56000 mg/L of salts.



Scheme 1: Slow release of CTAB in response to the ions existing in the solution which triggers the ion exchange mechanism

2.1 Introduction

Crude oil is by far the most utilized energy resource around the world. It accounts for up to 35% of the energy consumed in 2017 according to British Petroleum (BP, 2018). There are 3 stages for recovering oil. Primary which relies mainly on the reservoir energy to produce oil. In the secondary stage, because of the decline of the reservoir pressure, water and/or gas is usually injected to retain the pressure and increase the production of hydrocarbon.¹ Tertiary recovery accounts for using either thermal or nonthermal methods. Thermal methods have been implemented since 1950. Thermal methods are best used for heavy oil fields.² The nonthermal methods include utilizing gas and chemicals either before or post seawater flooding. Example of gas flooding includes CO₂ combined with water in a Water Alternating Gas (WAG) mode.³ Another means of nonthermal flooding include the injection of chemicals such as surfactants to increase the capillary number and/or improve the mobility ratio. The capillary number is a function of viscosity, velocity of displacing fluid and interfacial tension and is given by $N_c = \frac{\mu v}{\sigma}$. One of the ways to increase the

capillary number, and hence displace the residual oil, is by decreasing the interfacial tension, accomplished typically by utilizing surfactants.²

In recent years, there have been intensive efforts to formulate chemicals that could enhance oil recovery beyond the saturation limit. This requires agents to be able to change the forces that hinder the oil in the reservoir. For example, it has been studied and reported that after a long time of production, the reservoir wettability changes from favorable water-wet or mixed-wet region to oil-wet.⁴ Hence, in order to recover the oil, the chemicals need to change the wettability from oil-wet to water-wet.

Several publications reported that surfactants enhance oil recovery. Moreover, others demonstrated that the use of polymers and surfactant improved the mobility ratio and increased oil recovery.⁵⁻⁸ However, the use of bare surfactants has several drawbacks such as high rock adsorption, which will impose economic challenges, and instability at harsh reservoir conditions such as high temperature and concentration of salt. Overcoming these challenges usually is accomplished by injecting a large amount of surfactants to enhance oil recovery which may become uneconomic.⁹ To overcome this issue, a possible solution is to encapsulate and controllably deliver surfactants for better EOR performance.

Incorporating nanoparticles (NPs) into petroleum reservoir has been recently heavily pursued to give rise to a significant increase in oil recovery. Arab-D Dots (A-Dots), which are carbon fluorescent nanoparticles of size in the order of 5-10 nm, were field tested in harsh environment of temperatures up to 100 °C and salinity up to 120,000 PPM and demonstrated extraordinary stability.¹⁰ Furthermore, Alaskar and Kosynkin (2016) reported successful field deployment of the A-Dots, that were able to

travel 500 m in the harsh environment.¹¹ Moreover, several authors have conducted experiments that utilized organic and inorganic nanoparticles and demonstrated their efficacy in wettability alteration and reducing the interfacial tension. For example, Amr and coworkers have demonstrated a new class of NanoSurfactants with sizes of 10-60 nm that achieved 7% extra oil recovery from the oil initially in place.⁹

There are only a few studies exploring the controlled slow-release in the oil industry. Nourafkan et al. (2018) reported reducing the surfactant adsorption by 50% when using nanocarriers for Sodium Dodecyl Sulfonate (SDS) and achieved enhancement of 8% of oil recovery.¹² However, previous studies did not address the kinetics of slow release of surfactant from porous materials to concentrated brine solution that simulates injected water. Moreover, no clear quantification of the amount of surfactant released is reported. The slow release of surfactant for oil recovery application is attractive since it can potentially minimize the loss of surfactant due to adsorption and provide a better stability of the surfactant in the harsh reservoir conditions. Moreover, the slow release of surfactant molecules ensures maintaining the activity of the material as it travels in the reservoir for longer distances.

Cetyltrimethylammonium bromide (CTAB) is a cationic surfactant that has demonstrated an outstanding performance for EOR applications. For example, Standnes and Austad (2000) have studied the cationic surfactant consisting of different chain lengths and concluded that it could enhance the oil recovery.¹³ Moreover, the performance of CTAB and other anionic and nonionic surfactant was assessed by contact angle and spontaneous implementation experiments and it was concluded that the cationic surfactant had a better performance.¹ The mechanisms they proposed is

that the cationic surfactant could form ion-pair with the carboxylic group present in crude oil which mobilized it from the solid surface. Moreover, other researchers have concluded that the interfacial properties of silica NPs could be improved by surface functionalization by CTAB. For instance, it was reported that CTAB could reduce the interfacial tension of oil/water interface from 50 mN m^{-1} down to less than 10 mN m^{-1} .¹⁴ Therefore, CTAB is a good candidate for EOR applications and its encapsulation into compatible nanosized capsules is an attractive idea to control its release and performance.

In this work, a scalable and facile fabrication of nanosized capsules for controlled slow-release of surfactants is described and its applicability to oil field application is demonstrated. The system is based on the self-assembly of surfactants in an inorganic material. The material resulted from this synthesis route was first proposed by Beck and coworkers.¹⁵ Its unique structure and simple synthesis make it attractive for several research areas. The resulting nanoparticles have mesopores and are referred to as mesoporous silica nanoparticles (MSNs). There are different classes of the MSNs one of which is called Mobil Crystalline Material or Mobil Composition of Matter (MCM-41). It is characterized by having a tunable pore size that ranges from 2-10 nm, large surface area and relatively simple methods to implement surface and internal modifications.^{16,17} MCM-41 has been widely studied as a template for drug delivery,¹⁸⁻²⁰ and catalysts.^{21, 22} The utilization of MCM-41 in drug delivery and catalysis usually starts by eliminating the surfactant from the template and then loading the required molecules into the template. In contrast, in our system, we utilize

for the first time the readily available surfactant inside the mesopores and propose a controlled release mechanism for it at oil reservoir conditions.

As such this is the first report on using MCM-41 as silica nano-carrier to control the release of surfactant for EOR applications. The MCM-41 showed resistant to the highly saline water mainly due to the silica shell stability. Almost negligible release was noticed at salts-free brine. In saline brine, the ions trigger the controlled slow-release of surfactant molecules. To that end, MCM-41 is most-likely best suited for ions-responsive nano-carrier to slowly release surfactant for EOR. The fact that the ions are readily available in the reservoir makes this approach more compelling. Moreover, we demonstrate how the nano-silica capsules maintain their size even when being mixed with high salinity water.

2.2 Experimental Section

2.2.1 Materials

Reagents: Cetyltrimethylammonium Bromide (CTAB), Tetraethylorthosilicate (TEOS), Sodium Hydroxide (NaOH), Sodium Chloride (NaCl), Calcium Chloride Dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$), Magnesium Chloride Hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), Sodium Sulfate (Na_2SO_4) and Sodium Bicarbonate (NaHCO_3) were purchased from Sigma Aldrich and used as received without further purification.

2.2.2 Synthesis

The brine formulation is shown in **Table 1** and was similar to that proposed in the literature.²³ The salts were added to 1 L of 18.2 MQ water and stirred at room temperature until the mixture became homogenous. The synthetic seawater was used as is without further purification.

Table 1: the amount of the salt used in the preparation of the salinity water used in the release experiments

Compound	NaCl	CaCl ₂ .2H ₂ O	MgCl ₂ .6H ₂ O	Na ₂ SO ₄	NaHCO ₃
Weight (g)	41.04	2.384	17.645	6.343	0.165

To synthesize the porous nano-sized capsules containing CTAB, we followed the procedure of synthesizing MCM-41 as described in the literature.²⁴ Briefly, the CTAB was dissolved in 480 ml of 18.2 MQ water. The mixture was stirred until all the CTAB dissolved. 2 M NaOH solution was prepared in 18.2 MQ water and 3.5 ml was added to the beaker containing CTAB and water followed by adjusting the temperature to 80 °C. After that, 5 ml of TEOS was added dropwise while maintaining vigorous stirring of the solution. The mixture was kept stirring for 2 hours. The resultant white precipitate was collected, washed several times with deionized water and centrifuged at 9000 RPM for 15 minutes. The powder was then dried at 50 °C for two days.

2.2.3 Methods

Thermogravimetric analysis (TGA) was conducted under atmospheric conditions and a flow rate of 10 ml/min. The decomposition of the organic material is then used to assess the remaining organic content in the capsules. X-ray diffraction (XRD) analysis was performed to study the ordered porosity of the material. Scanning Electron Microscopy (SEM) and Transition Electron Microscopy (TEM) images were obtained to analyze the size and morphology of the resulted particles. Zeta Potential Measurements and Dynamic Light Scattering Measurements were carried out to determine the surface charge and the size of the particles.

Release experiments were conducted by dissolving 10 mg of the encapsulated surfactant in 20 ml of seawater. The solution was kept stirring to simulate the dynamic conditions of the reservoir, where fluids are in constant movement. Also, it is essential to avoid the build-up of the concentration gradient on the nanoparticles. After that, the sample was centrifuged at 8500 RPM for 15 minutes. The powder was placed in the oven at 50 °C to dry. The dried powder was then analyzed utilizing TGA to determine the amount of surfactant remaining in the capsules indicated by $M(t)$, which is the amount of surfactant released at time t . This amount is compared to the initial amount of encapsulated surfactant M_o and the released percentage is calculated as follow:

$$\text{Released CTAB Surfactant (\%)} = \frac{M_o - M(t)}{M_o} \times 100 \quad 1$$

2.3 Results and Discussion

2.3.1 Characterization

The synthesis of the mesoporous silicate materials combines both the sol-gel and surfactant sciences. The formation of MCM-41 is suggested to follow a liquid crystal templating mechanism. The cationic surfactant form micelles and then the silicate will condense around the surfactant micelles which had already formed hexagonal array. Finally, the randomly ordered composites will form a highly packed hexagonal arrangement which is an energetically favorable process. The formation of the mesophases is by the interactions of the organic and inorganic molecules. In the case of ionic surfactant S^+ interaction with the inorganic species I^- by Coulombic attractions. It is this strong electrostatic interaction that would lead to the formation of

a matrix with well-defined pores.²⁵ However, previous researchers extracted the surfactant to create template free mesopores.

In our approach, we utilized this mechanism as a method to encapsulate CTAB into porous nanosized capsules and slowly release it into the bulk solution. While this material is composed mainly of silicon dioxide and the surfactant, the decomposition of the material would be utilized to indicate the amount of the surfactant encapsulated. According to **Fig. 1**, the weight loss from 30 °C until 150 °C is a result of the desorption of the physically adsorbed water.²⁴ Moreover, CTAB is reported to start decomposing at 200 °C.²⁶ Hence, the weight loss from 200 °C to 300 °C is utilized to know the initial amount of surfactant in the nanocapsules. As shown in the figure, approximately 40% of the total mass of the material is organic content. Since CTAB is the only organic source used in the synthesis, this is used to directly assess the amount of CTAB encapsulated in the mesopores. Also, this interval is utilized to quantify the amount of surfactant released after suspension in seawater since the decomposition of silicon dioxide is above 1000 °C.

The X-ray Diffraction is a technique used to elucidate the formation of ordered and long-range porous structure. Unlike amorphous silica NPs which are rigid and lack a well-defined shape exhibiting one distinct peak at 2Θ of 20° ,²⁷ the structure of MCM-41 depicts a well-defined hexagonal shape. The four peaks that are present at 2Θ of 2.2° , 3.8° , 4.4° and 5.8° in the XRD result shown in **Fig. 2** clearly illustrates the ordered porosity of the material with the surfactant in the porous spaces. It also indicates the long-range ordered mesoporosity of the particles. The presence of the four peaks is also used to prove the formation of a hexagonal array.²⁸ Moreover, TEM

image in **Fig. 3** of the powder clearly shows the ordered porous hexagonal structure, complementing the results obtained from the XRD. The SEM image shown in **Fig. 4** indicates the presence of hexagonal particles with a practically uniform size of 50-100 nm in diameter.

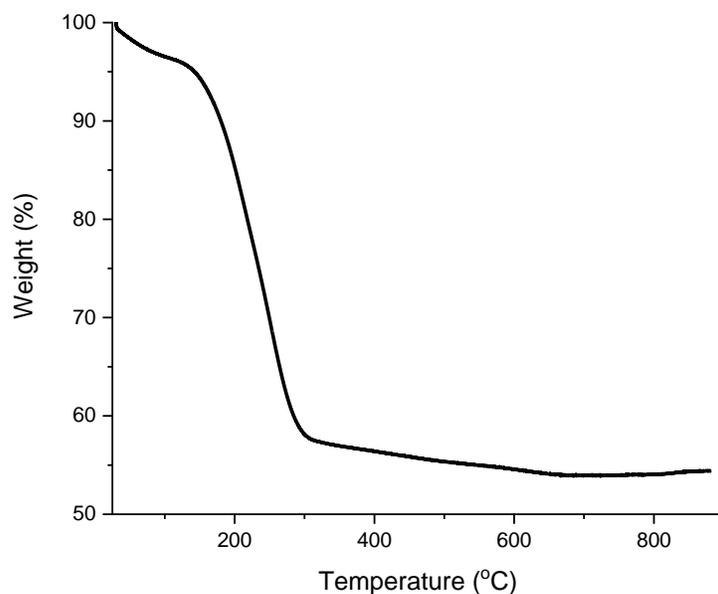


Figure 1: TGA results for the encapsulated surfactant indicates 40% of total organic content

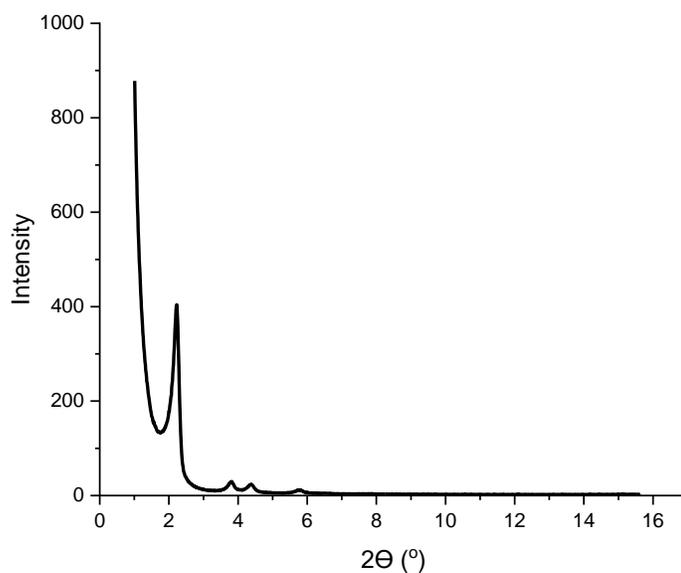


Figure 2: X-ray Diffraction pattern of MCM nanoparticles

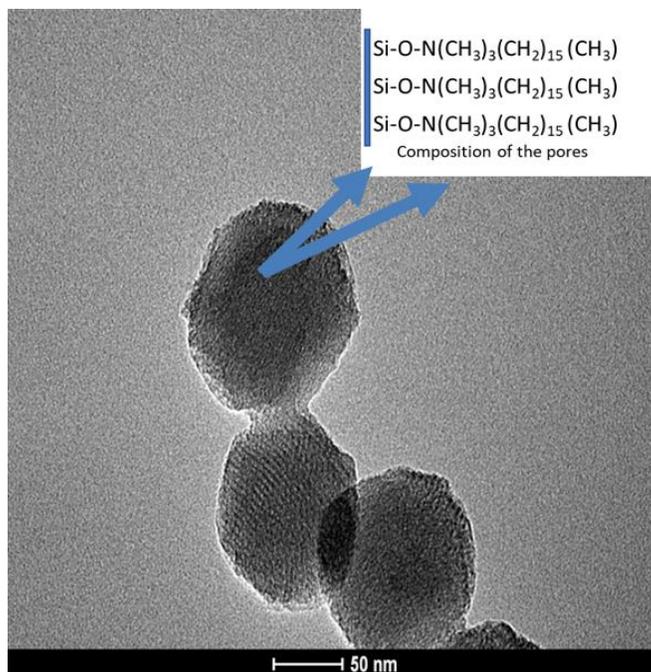


Figure 3: TEM image of the encapsulated surfactant showing the channels of the porous material

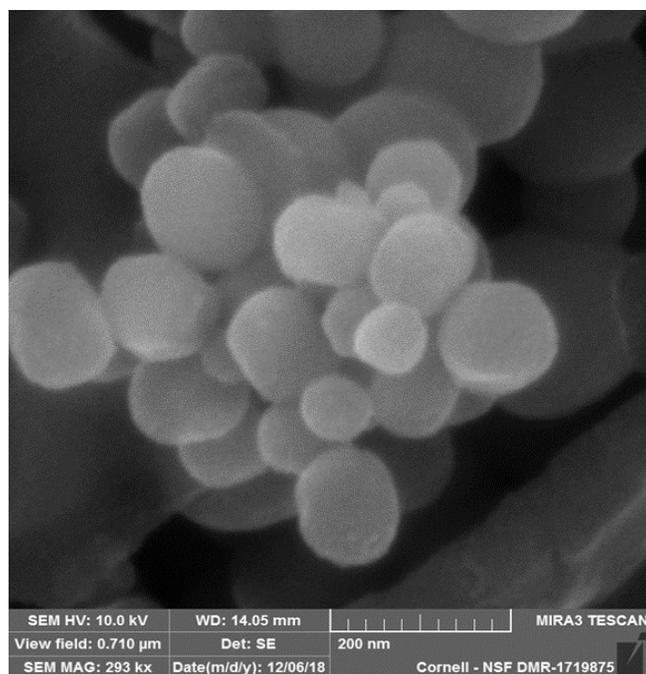
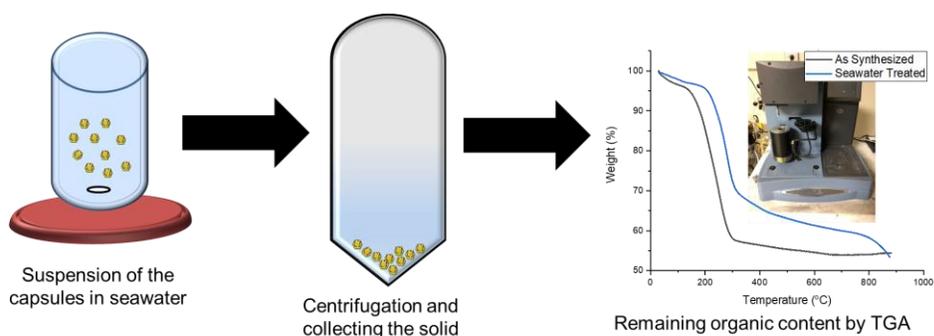


Figure 4: SEM images showing particles with hexagonal shape of size 50-100 nm

2.3.2 Release Experiments

As indicated earlier, the release experiments were conducted by mixing 10 mg of the encapsulated surfactant in 20 ml of brine. The sample was removed from the suspension and allowed to dry at 50 °C. Finally, the amount of organic content was determined by TGA. The process is shown in Scheme 2.



Scheme 2: Schematic Representation of the release experiments and quantification of the released surfactant

Fig. 5 shows the amount of CTAB released in 12 days. The release starts very slowly at 10% within the first day. It then continues to increase gradually until it stabilizes at about 50% within the first 12 days of experiments. Despite the burst release that occurred within the first hours, the particles maintain a slow release profile for two weeks ensuring controlled and sustained delivery mechanism of the surfactant. This unique behavior of the slow release of CTAB over the course of 12 days supports the idea of the potential use of this material as a carrier for surfactant that can be delivered efficiently in the reservoir without being lost quickly due to adsorption or instability. The release of surfactant, however, could be even further controlled with the introduction of functional groups and modification of physical properties of the particles such as the pore volume and pore size. Such techniques have been investigated extensively in drug delivery, where it was shown that the release could be

controlled by the introduction of different surface groups,²⁹ and slower release was achieved by reduction of the pore size.³⁰

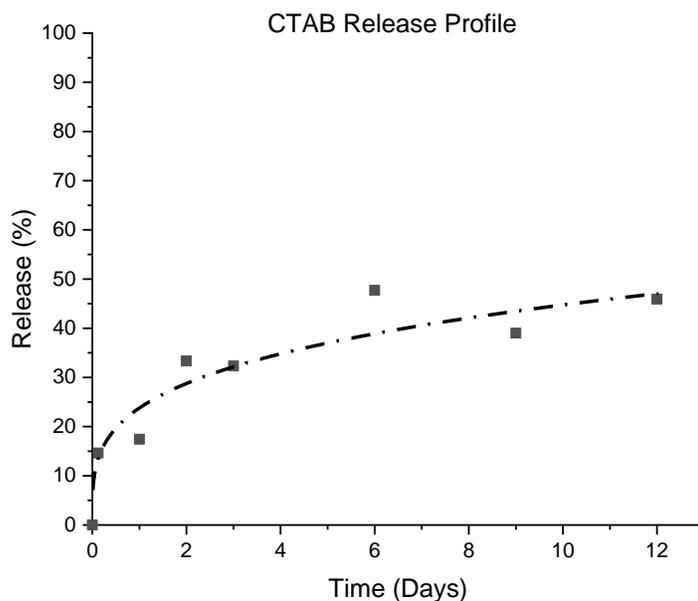


Figure 5: Release profile of CTAB over 12 days

Moreover, with minimum stirring speed, the particles maintained their dispersibility with the high salinity brine that is mixed with. As shown in **Fig. 6**, the sample shows no apparent phase separation when mixed with high salinity water at both room temperature and 65 °C.

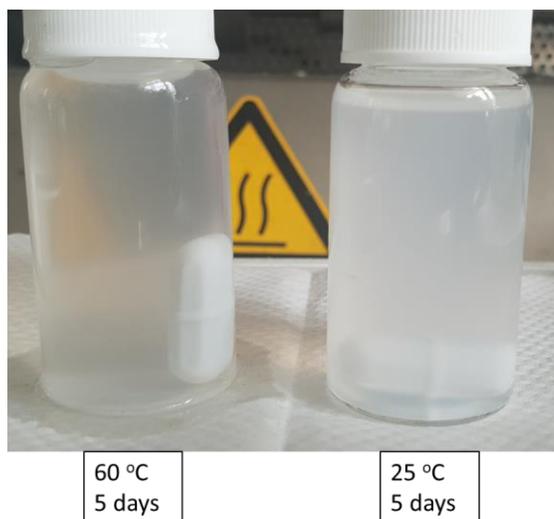
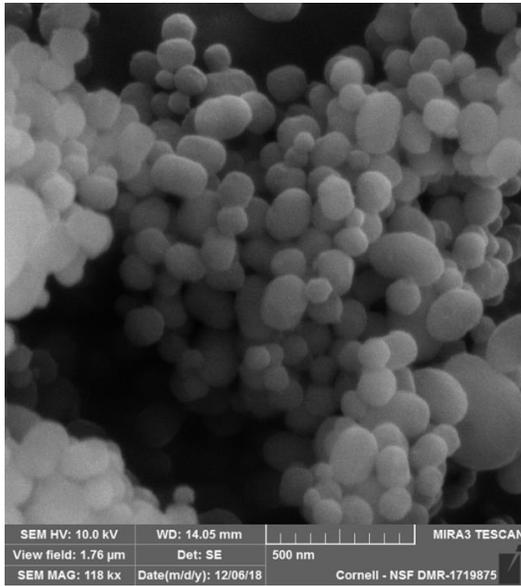
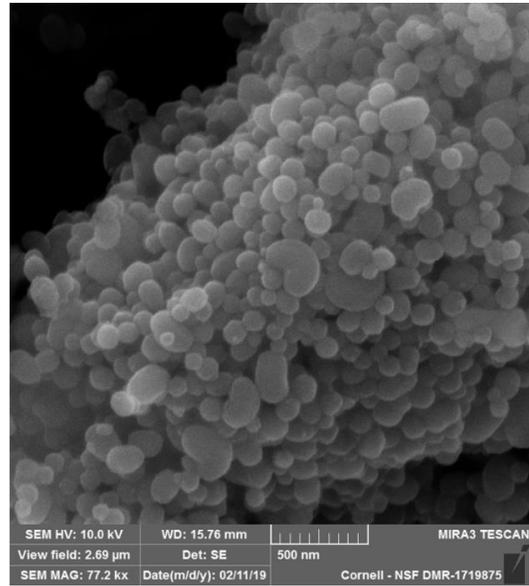


Figure 6: The dispersibility of the encapsulated surfactant with high salinity brine at both high temperature at room temperature

One limitation that some nanoparticles systems have shown upon mixing with divalent salts, is particle agglomeration. A phenomenon that is not desirable when using nanoparticles to the challenging reservoir environment as they will plug the formation causing more decline in oil production. In contrast, our approach shows that the particles actually maintain their size by SEM and DLS as shown in **Figs. 7 and 8**. One reason for this stability is the dominant negative charge at the surface of the particle. Previous studies³¹ indicated that the predominant groups at MCM-41 particles are silanol groups. The zeta potential in **Fig. 9** indicates that the charge on the surface of the particle is about -25 mv.



Before release



After release

Figure 7: SEM images showing the capsules before and after the release of surfactant

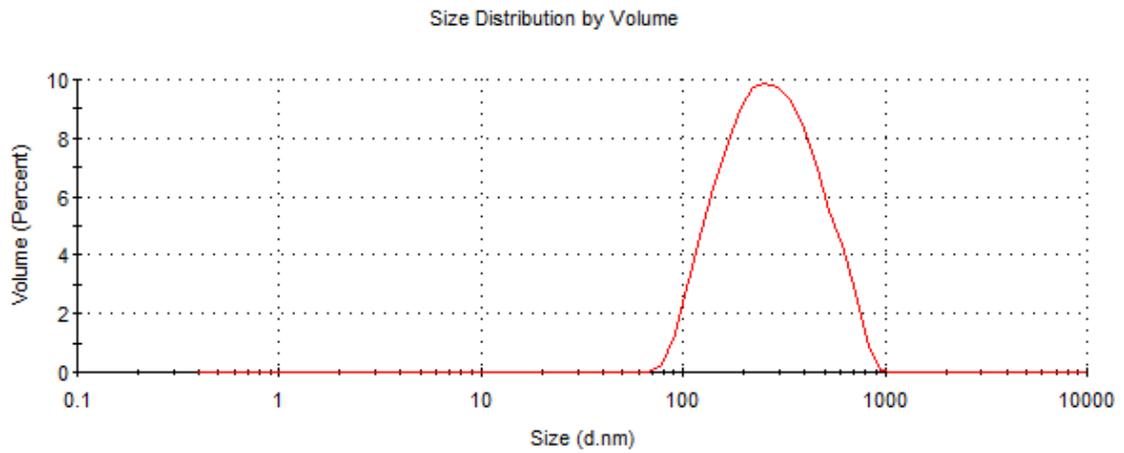


Figure 8: DLS show the particle maintain size of 200 nm upon mixing with high salinity brine solution

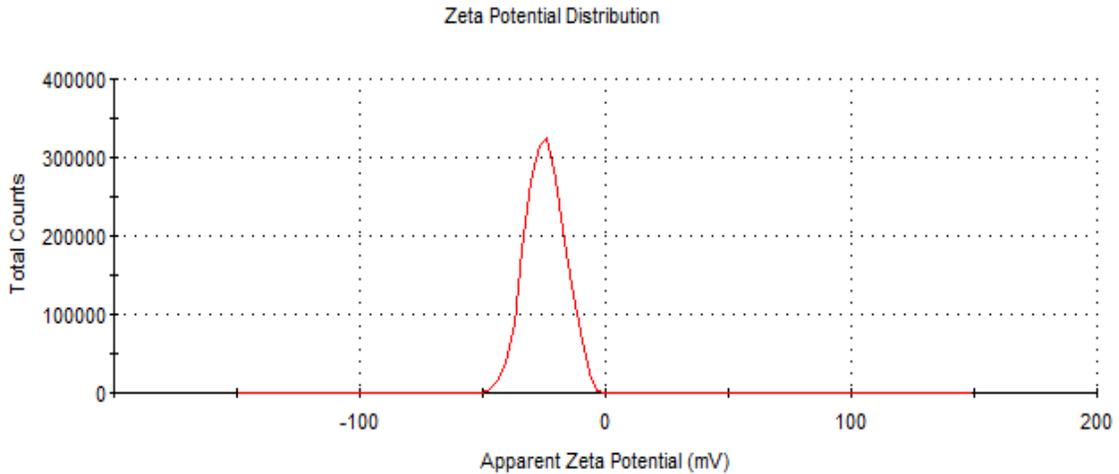


Figure 9: Zeta Potential of the nanosized porous particles indicate dominant negative charge

The SEM images after the release experiment indicate that the release does happen as a result of diffusion of surfactant molecules from the porous media to the bulk fluid. Moreover, it certainly indicates that the release does not occur because of the dissolution of the particles. In contrast, the surfactant migrates from the porous structure to the bulk fluid. Most importantly, this shows that the particles do maintain their size even when they are mixed with high salinity brine.

Within three days 35% of the surfactant originally encapsulated is released. The release profile might be considered as a burst release and it is certainly applicable whether the nanoparticles are injected in a producer then allowed to release around the well, or in an injector where they will travel in the reservoir. Asphaltene precipitation tends to occur near-wellbore area of producers where the pressure decline is noticeable.³² As a result of asphaltene deposition, the wettability of the reservoir tends to be more oil-wet.³³ It has been shown¹ that CTAB is considered as one of the best wettability modifiers. Therefore, the slow release of CTAB from the nano-porous

particles around the wellbore of an oil-wet formation will result even in further reach in the reservoir.

$$\frac{\partial c_A}{\partial t} = D_{AB} \frac{\partial^2 c_A}{\partial z^2} + x_A (N_A + N_B) \quad 2$$

C_A : Concentration of CTAB ($\frac{mole}{ml}$)

x_A : Mole fraction of CTAB

N_A : Flux CTAB

N_B : Flux of seawater

Here, we assume that the mole fraction of CTAB is very low compared to that of water and hence no contribution of convective flux to the continuity equation. Moreover, because our material remains the same (no swelling or dissolution) after the release as shown in Fig. 7, the diffusion coefficient is constant.²⁰ Several models were proposed to study drug diffusing from the MCM-41 matrix. One of the widely used models to study drug release from the porous medium is Higuchi model.³⁴ The model assumes pseudo steady-state and that the amount of drug initially present is larger than the solubility of the drug in the system. The equation Higuchi employed is:

$$M(t) = \sqrt{D_{eff}(2C_o - C_s)C_s t} \quad 3$$

D_{eff} : Effective diffusion Coefficient ($\frac{cm^2}{min}$)

C_o : Initial Concentration per unit volume ($\frac{mg}{ml}$)

C_s : Solubility of the drug (encapsulated material) in the system ($\frac{mg}{ml}$)

t: time (min)

And could be simplified to the following:

$$M(t) = k\sqrt{t} \quad 4$$

Fig. 10 shows the fit of the released surfactant versus the square root of time as suggested by the Higuchi model for a non-moving boundary condition. The experimental data follow clearly the model and the pre-factors of the $t^{1/2}$ are a function of solubility constant of the CTAB in brine, diffusion coefficient and the area of the particle. The previously studied systems using this model showed deviations from the equation as time increases.²⁰ However, our data indicate that the release profile follows the linearized Higuchi model up to 6 days and then deviates from it as a result of reaching the maximum release possible at the conditions of the experiment. The Higuchi model does not take into account the leveling of the release after a given time and it just describes the profile as a linear increase with time. To the best of our knowledge, this is the first proposal to utilize the Higuchi model, which has been thoroughly utilized in studying the diffusion of drugs, for the release of surfactant from porous nanomaterial at high ionic concentration. Since the model describes the data well, it could be further utilized to optimize the system for controlling the release of surfactant for oil field applications. For example, from the linear fit, one can obtain the diffusion coefficient for varying physical properties of the particles, and then design fit-for-purpose porous particles that could be deployed to control the release of surfactant for EOR applications.

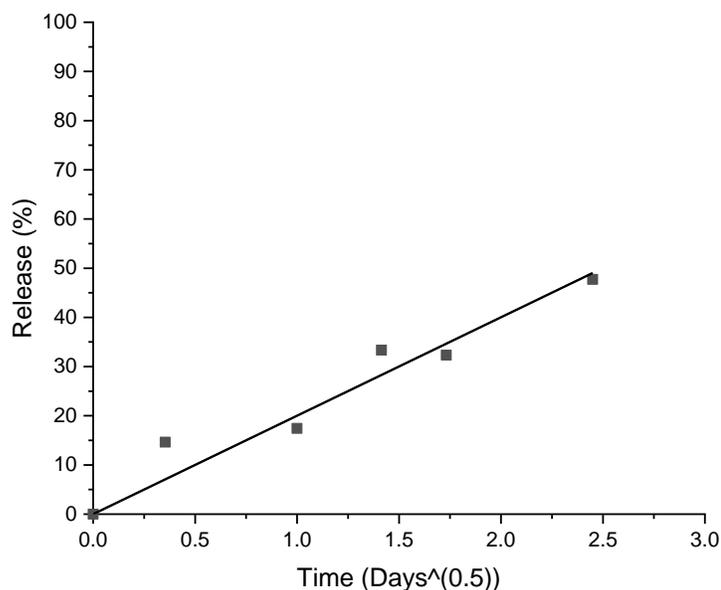


Figure 10: Model fit of the release data

The release of the surfactant is driven by the readily available ions in brine. The ions that are abundant in an oil reservoir are the driving force for the release of surfactant molecules by reverse ion exchange. The nano-sized porous particles would only release surfactant upon encountering the ionic environment that is present in the brine and in the oil reservoir. To further investigate this theory, 10 mg of the material was mixed with 20 ml DI water and left stirring overnight. The sample was then centrifuged and dried at 50°C overnight. As shown in **Fig. 11**, the mass loss between the as-synthesized nanoparticles and the one aged for one day are identical. When mixed with seawater, the nanosized particles released about 20% compared to none when mixed with DI water. This indicates that the release is due largely to the ions present in brine.

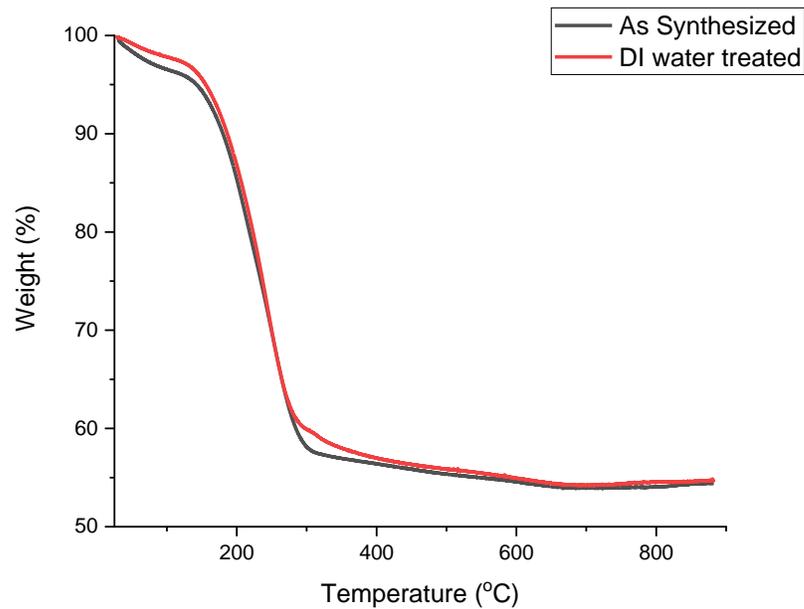


Figure 6: The weight loss comparing a sample aged with DI water for 1 day (red) and the sample before it is mixed with water (black)

Conclusion

We presented a simple yet innovative approach based on nanosized porous particles for controlling the release of surfactant. SEM and TEM indicate that the particles have a hexagonal structure with ordered mesopores, which is also confirmed by XRD. Zeta potential shows that the dominant surface charge on the particle is negative which we reason to be a result of ionized silanol groups. The surfactant molecules released in the fluid reached up to 46% in 12 days. The release occurs as a result of ions exchange with surfactant molecules encapsulated in the mesoporous sites of the framework. The ions which drive the release exist in abundance in oil field water. SEM images reveal that the release happens from the matrix and not as a result

of dissolution. We further utilize the Higuchi model to show that the release follows Fickian dynamics.

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CHAPTER 3

RESPONSIVE NANOSIZED CAPSULES FOR ACHIEVING ULTRALOW INTERFACIAL TENSION AND WETTABILITY ALTERATION

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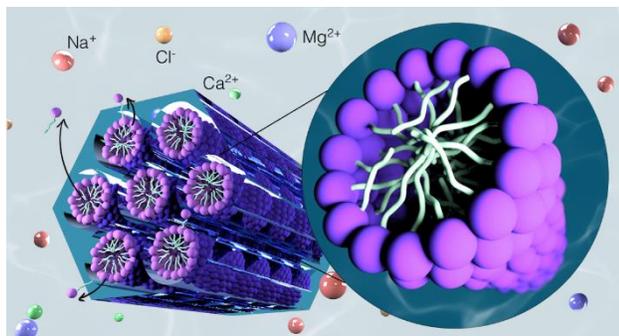
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Abstract

Engineered nanosized carriers for the slow release of surfactants utilizing structured mesoporous silica is reported. The release of surfactant molecules relies on the abundance of ions and high temperature conditions present in an oil reservoir. The results show that 50% of the surfactants encapsulated is released within 12 days at high temperature and salinity. In contrast, no release is observed when the nanosized capsules are suspended in deionized water. The mechanism by which the nanocarriers change the wetting forces is also studied. The released surfactant is responsible for the oil-wet to a water-wet alteration. Moreover, the liquid-liquid interactions were characterized via interfacial tension measurements. The CTAB released from the mesopores enhanced the adsorption of the nanocarriers to the oil-water interface resulting in an interfacial tension in the order of 10^{-2} mN m⁻¹.



Scheme 1: Slow release of CTAB in response to the ions existing in the solution which triggers the ion exchange mechanism

3.1 Introduction

Removal or recovery of oil, which is either attached to a solid surface or as an emulsion in water is an ongoing challenge. Oil present in the soil can become a continuous source of contamination for groundwater.^{1,2} Moreover, oil remains the most used fuel in the energy mix and efforts to improve recovery are critical. In both cases, efficient methods to remove and recover the oil are required.^{3,4}

Two important forces hinder the removal and recovery of oil: wetting forces and interfacial tension.^{5,6} Capillary forces allow the wetting phase to remain in the small pores where it prevents the entrance of the nonwetting fluid.⁷ Hydrocarbons could contain polar groups such as carboxylic acids that interact strongly with solid surfaces making them oil wet.⁸ Wettability alteration of the surface from oil-wet to water-wet is one of the main approaches for increasing oil production.⁹

Various methods have been explored to remove oil that is attached to a solid surface or present as a non-continuous phase in water. Surfactants are known for their effectiveness in recovery of oil and treatment of contaminated soil.^{1,6,10,11} Standnes et al. proposed that the negatively charged carboxylic groups in the oil form ion pairs with the surfactant molecules, which causes desorption of the oil attached to the rock

surface.¹² Moreover, a series of experiments concluded that the residual oil is governed by the capillary number, which is defined as:

$$N_c = \frac{\mu v}{\gamma} \quad 1$$

In the above μ is the viscosity, v is the velocity and γ is the oil-water interfacial tension. Hence, the reduction of the interfacial tension leads to an increase in the capillary number.^{13,14} One of the parameters of achieving lower IFT is the partition coefficient of the surfactant at the oil-water interface, which is based on several properties that include salinity, the molecular structure of the surfactant and oil, and temperature.¹⁵ Various studies have employed surfactants and achieved ultralow interfacial tension in the order of 10^{-3} mN m⁻¹.¹⁶⁻²¹

While adsorption of surfactants to the surface is essential for wettability alteration and partitioning in the oil-water interface is essential for achieving low interfacial tension, high adsorption of surfactant molecules makes the process inefficient in many applications.^{22,23} Nanomaterials have been proposed to aid the deployment of surfactants due to their size, which helps them permeate the pores. Another advantage is their large surface area and the ability to functionalize chemically their surface. The synergy between surfactant and nanomaterials have been explored for their potential to improve surfactant efficiency and reduce adsorption.^{24,25} For example, it was reported that when Tween-20, a nonionic surfactant, was employed with silica nanoparticles, the efficiency of removing diesel contaminated soil increased by ~50%.²⁶ Moreover, Ahmadi et al. reported the use of hydrophobic silica nanoparticles suspended in a solution containing surfactant, which resulted in

lowering the adsorption of surfactant from $14\text{mg/g}_{\text{rock}}$ to $4\text{mg/g}_{\text{rock}}$ on sandstone rock surface.²⁷ Similarly, Zargartalebi et al. reported that silica nanoparticles reduced the adsorption of anionic surfactant one order of magnitude.²⁸

However, the surfactants can be physically adsorbed on the surface of the particles, which exposes them to the harsh conditions such as high salinity and high temperature, which negatively affects their thermodynamic activity and stability over time. Also, the surfactant can form a bilayer on the surface of the particles which might prevent their adsorption at the oil-water interface. An alternative approach is required in order to develop a more efficient surfactant system.

Encapsulation of active molecules into compatible shells for targeting and drug delivery has been extensively explored for biomedical applications.^{29,30} More recently, researchers in the oil and gas industry have started exploring this concept for hydrocarbon reservoir applications. For example, Cortes et al. reported the fabrication of nanocapsules of two types of surfactants and they claimed an efficient reduction of IFT with an increase of the oil recovery by 23%.³¹ Moreover, Rosestolato and co-workers utilized beeswax as a lipid structure carrying nonylphenol ethoxylate surfactant and studied its performance for EOR applications by means of IFT and wettability alterations.³² However, the previous studies did not propose a mechanism by which the surfactant is released in the bulk fluid. Also, no previous quantification of the amount of surfactant released was provided nor highlighted the relationship between the released amount and the physical phenomenon observed. Most importantly, the physical adsorption of the surfactant to the surface or onto the carriers make them susceptible to losses in comparison with chemically attached surfactant in

the pores of nanoparticles. Our group recently proposed utilizing MCM-41 particles as carriers for delivering cetyltrimethylammonium bromide (CTAB). The slow-release was assessed in simulated reservoir conditions of high salinity and temperature.¹⁴

This work aims to investigate the use of nanocapsules containing CTAB to alter the wettability of hydrophobic silica and calcite surfaces. Moreover, we show that the wettability alteration is a result of the slow release of CTAB from the pores of the structured silica nanoparticles. The results show that this framework can achieve ultralow IFT and that the system is thermodynamically stable and maintains low IFT over a long period. Moreover, we provide a kinetic study to elucidate the mechanism by which the nanocapsules are adsorbed at the oil-water interface resulting in the reduction of the interfacial energy. Finally, we demonstrate that the nanosized capsules responsiveness to the presence of ions and the increase in temperature are responsible for lowering the interfacial tension and altering the wettability.

3.2 Experimental Section

3.2.1 Materials

Cetyltrimethylammonium bromide (CTAB) was purchased from TCI and used without further purification. Sodium chloride (NaCl), calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$), magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), sodium sulfate (Na_2SO_4), sodium bicarbonate (NaHCO_3), tetraethylorthosilicate (TEOS), and sodium hydroxide (NaOH) were purchased from Sigma Aldrich and used as received without further purification. Indiana limestone rock was kindly provided by ARAMCO, Boston Research Center, and was used to mimic the carbonate surface. Silicone oil

and crude oil were used to alter the surface properties of silica glass and carbonate.

Dodecane was used as a model oil for the interfacial tension measurements.

3.2.2 Synthesis

The nanocapsules were synthesized following the previously published method.¹⁴ Briefly, CTAB was dissolved first in 480 ml of 18.2 MQ water. Then, 3.5 ml of 2 M NaOH solution was added and the temperature was adjusted to 80 °C followed by the addition of 5 ml of TEOS to the mixture. After two hours, the white precipitate was collected by centrifuging and washed several times with deionized water. Finally, the powder was dried for one day at 50 °C. Seawater was prepared following the procedure reported by Afnan et al., which is common injection water for oil fields.³³

3.2.3 Apparatus and Methods

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were performed on MIRA Tescan and Tecani T12 microscopes, respectively. Thermogravimetric analysis (TGA) was conducted using TA instrument Q500 under atmospheric conditions. FT-IR spectra were collected on a Bruker Vertex Vacuum spectrometer. Contact angle measurements were performed on a Contact Angle Tester by Biolin Scientific using the sessile drop technique. Interfacial tension measurements were obtained using a Spinning Drop Tensiometer (SDT) by Kruss.

3.3 Results and Discussion

3.3.1 Characterization

TEM (**Fig. 1**) and SEM (**Fig. 2**) analysis of MCM-41 nanoparticles showed uniformly distributed, non-aggregated hexagonal nanoparticles with sizes of 50-100 nm. Note that while for most studies using MCM41 mesoporous silica the surfactant template is removed in order to open the pores and access the large surface area.^{34,35} In this study, we keep the surfactant and study its release and delivery under various conditions. The composition of the hybrid NPs is 40% organic as shown in **Fig. 3** by the weight loss from 200 °C to 400 °C. The presence of MCM-41 is confirmed by FTIR spectroscopy (**Fig. 4**) and specifically the presence of a peak at 1070 cm^{-1} , which is attributed to the Si-O-Si stretching vibration. In addition, the presence of the surfactant is confirmed by the peaks at 2900 cm^{-1} attributed to the alkyl groups.

In our previous report, we demonstrated the slow release of surfactant at room temperature.¹⁴ However, it is essential to investigate the release at a higher temperature to simulate the subsurface conditions.¹⁶ As shown in **Fig. 5**, despite being suspended in high salinity and high-temperature environment, the particles maintain the slow release over 9 days, where only 50% of CTAB is released. These results prove that the NPs are stable under harsh conditions and that they can be deployed for wettability alteration and IFT reduction.

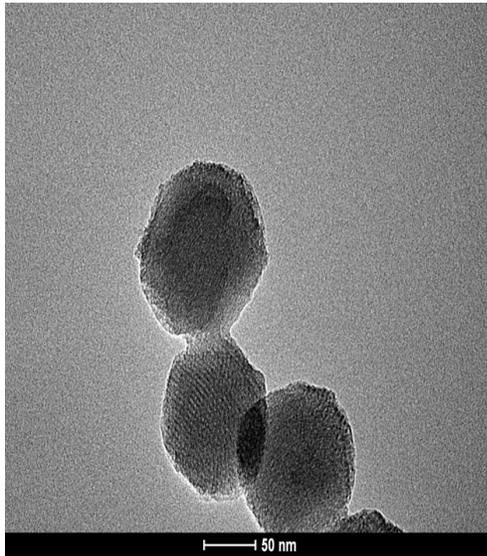


Figure 1: TEM images showing the nanosized porous capsules containing CTAB surfactant

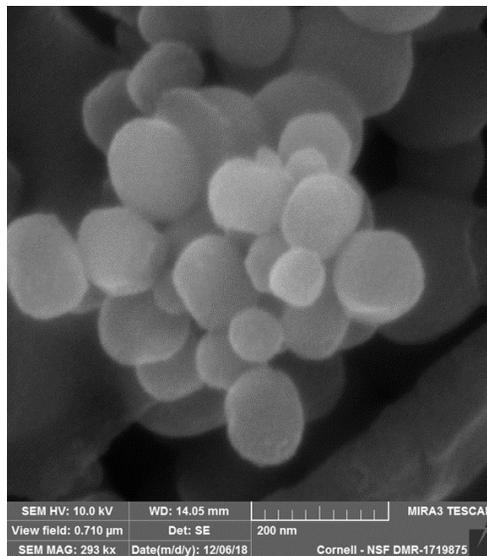


Figure 2: SEM images indicating 2-D hexagonal structure of the particles

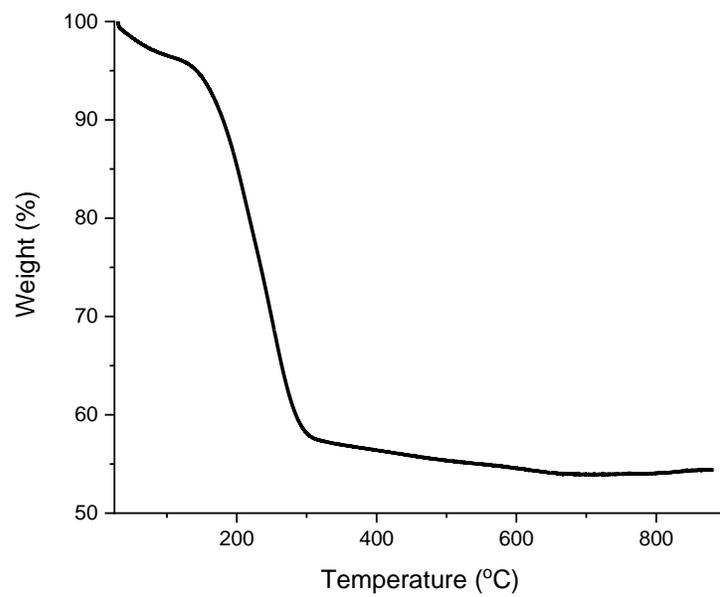


Figure 3: TGA indicates 40% of surfactant encapsulated in the particles

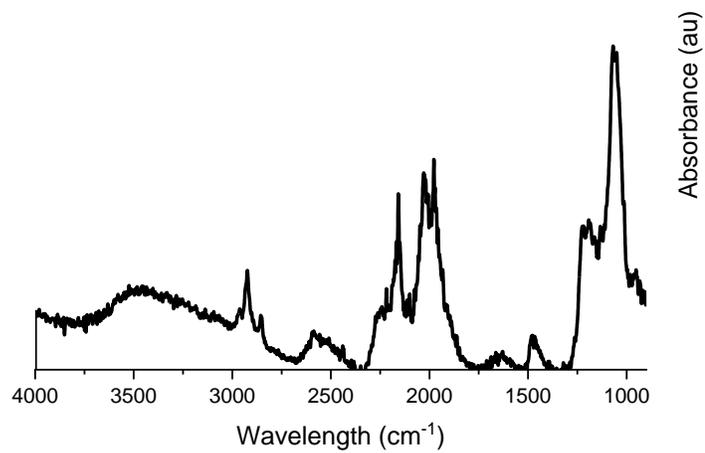


Figure 4: FTIR spectrum showing the peaks of Si-O-Si and alkyl groups

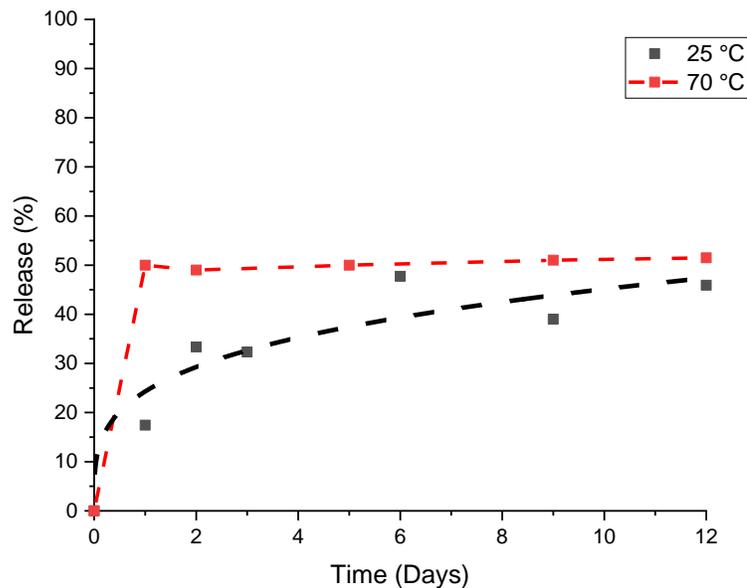


Figure 5: release profile for CTAB

3.3.2 Wettability Alteration

CTAB has been extensively used for wettability alteration.^{12,36-38} However, rock adsorption is a key limitation of this surfactant, which makes the process less effective and adds to the cost.^{6,22} Hence, encapsulating CTAB molecules into nanosized porous particles and slowly releasing them in the reservoir is an attractive alternative. In order to show that the CTAB release alters the wettability of surfaces experiments on both silica glass and carbonate were performed.

3.3.2.1 Wettability Alteration of Silica Surface

VWR micro-cover glass was used to mimic sandstone reservoirs and the wetting behavior of different fluids. The glass has a contact angle of 75° prior to aging in oil. After functionalization with oil, the contact angle becomes 110° (**Fig. 6**). The

FTIR spectrum, **Fig. 7**, confirms that the change in contact angle is a result of alkyl groups attached to the glass surface.

When a drop of seawater is placed on the glass, the contact angle does not change and it remains hydrophobic. In contrast, a drop of the seawater containing the suspension of the MCM-41 nanocapsules alters the wettability momentarily and the contact angle decreases up to 20° in 55 minutes (**Fig. 8**).

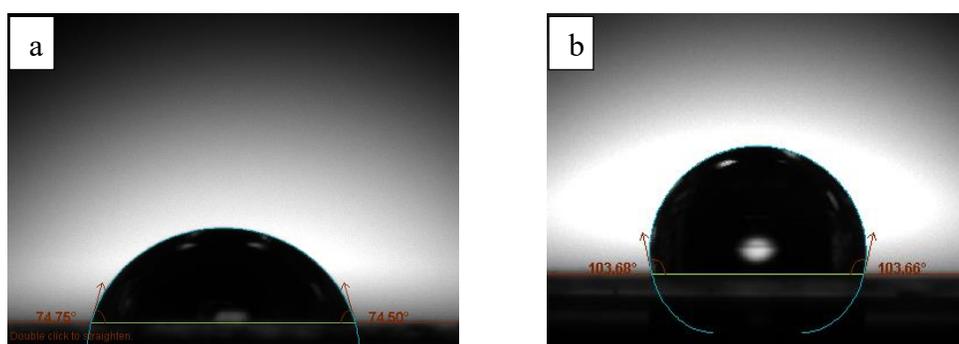


Figure 6: Contact angle of the glass sheet using a drop of synthetic seawater. a) before aging in silicon oil b) after aging in silicon oil

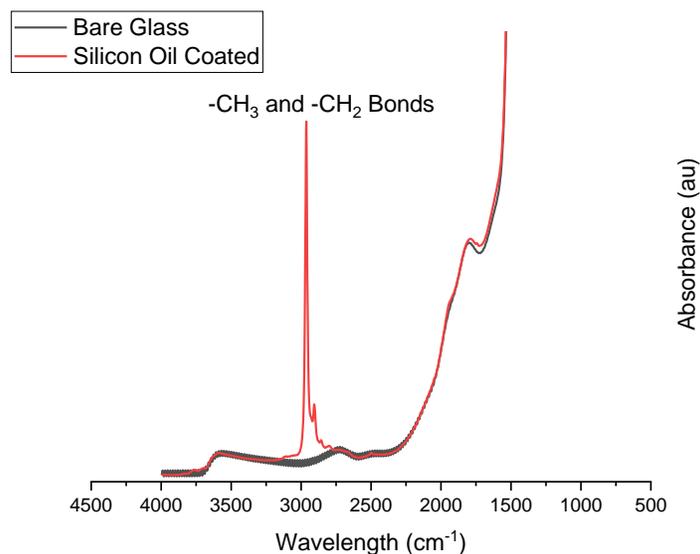


Figure 7: FTIR Spectrum shows alkyl groups attachment to the glass surface

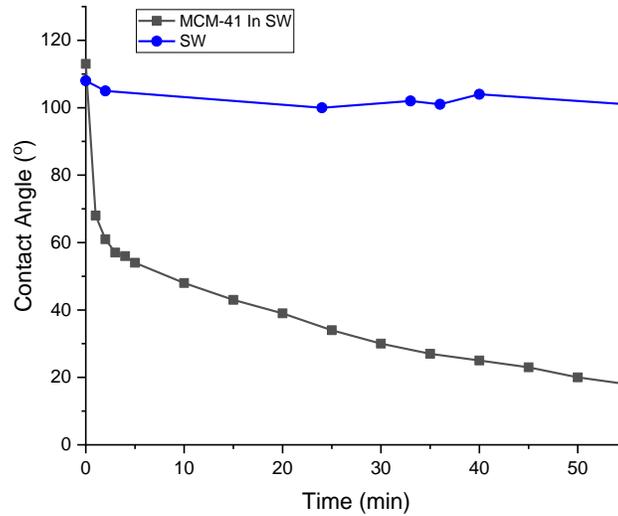
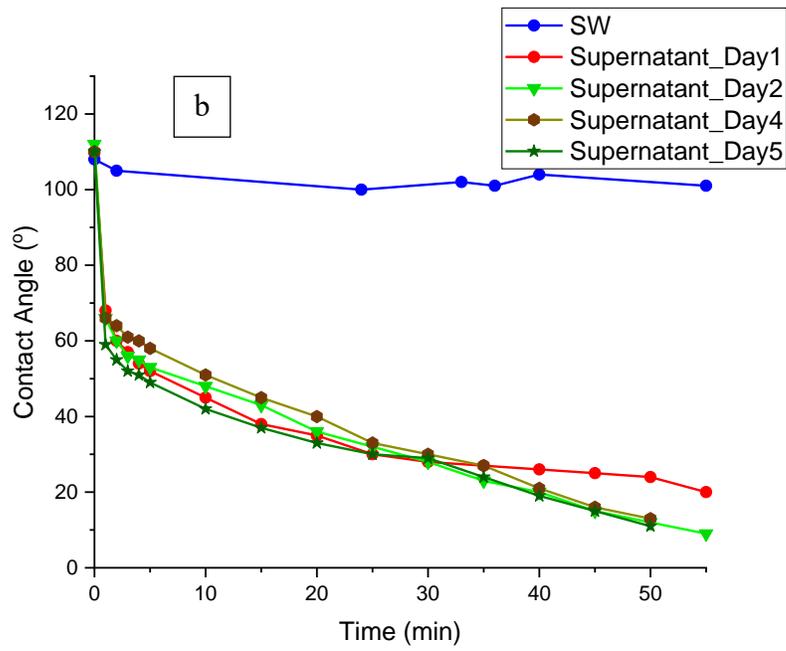
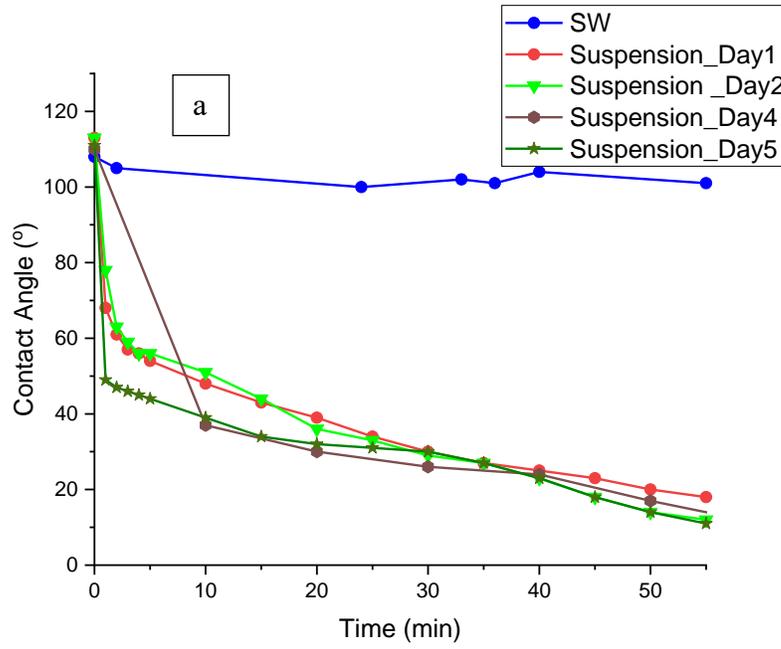


Figure 8: Contact angle profile for seawater (blue) and MCM-41 particles suspended in seawater (black)

As shown in **Fig. 9a** and **b**, the MCM-41 nanoparticles are able to provide sustained release over some time. To demonstrate that the release of the surfactant is responsible for the wettability alteration, a drop of the supernatant after removal of the nanoparticles was placed on the glass. As shown in **Fig. 9b**, the reduction of the contact angle is a result of the surfactant that is released in the seawater. It is also worth mentioning that when the micro-glass was also aged in crude oil, a similar profile was obtained indicating that the system is not dependent on the type of oil used (**Fig. 9c**).



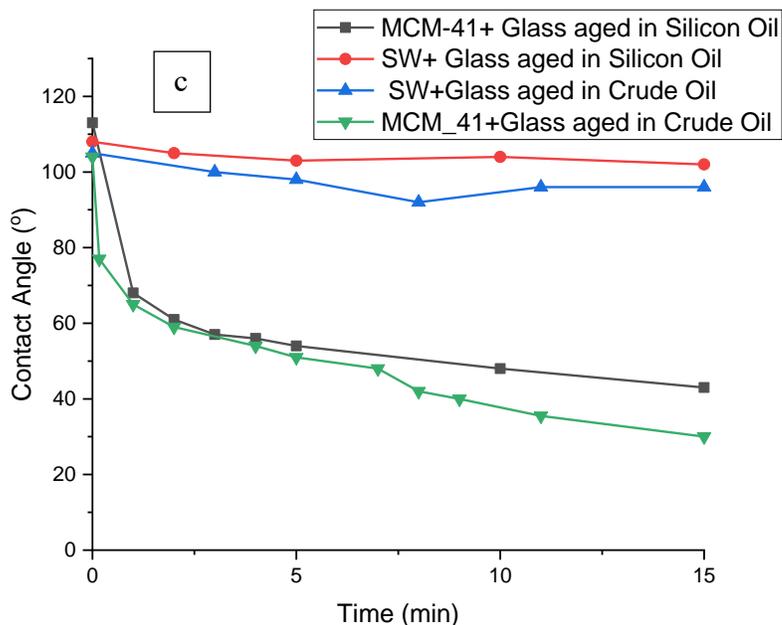


Figure 9: The contact angle both the suspension (a) as well as the supernatant(b) and c) the contact angle profile when the micro-glass is aged in crude oil

3.3.2.2 Wettability Alteration of Carbonate Surfaces

Calcite surfaces are common underground. The surface of calcite is known to be positively charged below a pH of 9.³⁹ As a result, the negatively charged groups in crude oil interact strongly with the positively charged calcite surface.^{1,40,41} Therefore, part of our study aimed at qualifying the new delivery system for use with calcite reservoirs. As shown in the FT-IR spectrum (**Fig.10**), the presence of the alkyl groups' vibrations confirm that the crude oil adsorbed successfully to the calcite surface shown in **Fig. 11**. The calcite surface became hydrophobic after aging in crude oil as shown in **Fig. 12** where the contact angle of the seawater drop increased from 40° (**a**) to 110° (**b**). The pellet was then aged in either seawater or MCM-41 particles suspended in

seawater. After one day, a drop of seawater was placed on the pellet. As seen in **Fig. 12 c and d**, aging in seawater did not alter the wettability. However, when the pellet was aged in seawater containing MCM-41 particles, the surface became hydrophilic and the contact angle decreased to 33°.

Several previously published reports have studied the mechanism by which CTAB alters the wettability. For example, Hou et al.³⁶ examined the wettability alteration caused by CTAB for both quartz and mica plates. They found that the negatively charged carboxylic acid groups interact with the positively charged surfactant to form an ion pair. The ions pairs are then solubilized to form micelles. They have observed also that the zeta potential of the plates treated with CTAB changed from negative to positive indicating the adsorption of CTAB to the solid surface. A similar conclusion was also made by Standnes and Austad,^{12,38} who studied the effect of utilizing CTAB as a wettability alteration agent. They noted that the carboxylic group in the oil phase allows better partitioning of the CTAB surfactant by means of forming ion-pairs.

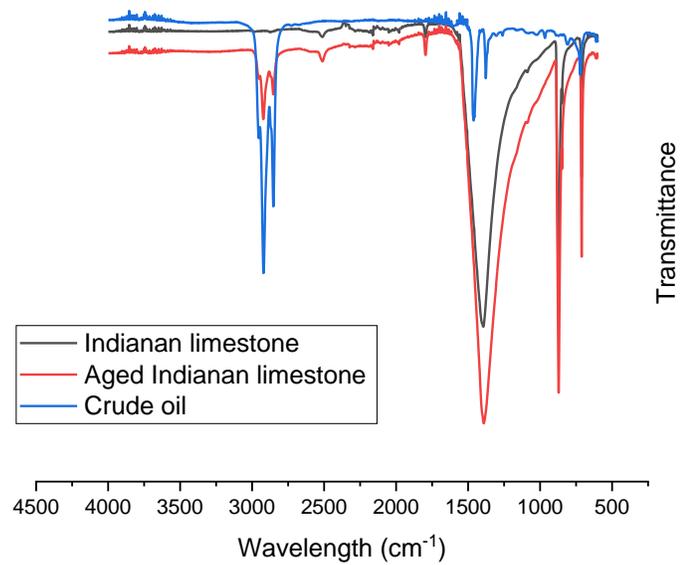


Figure 10: FTIR for the carbonate before and after aging with oil



Figure 11: The Indiana limestone pellet formed by uniaxial compaction

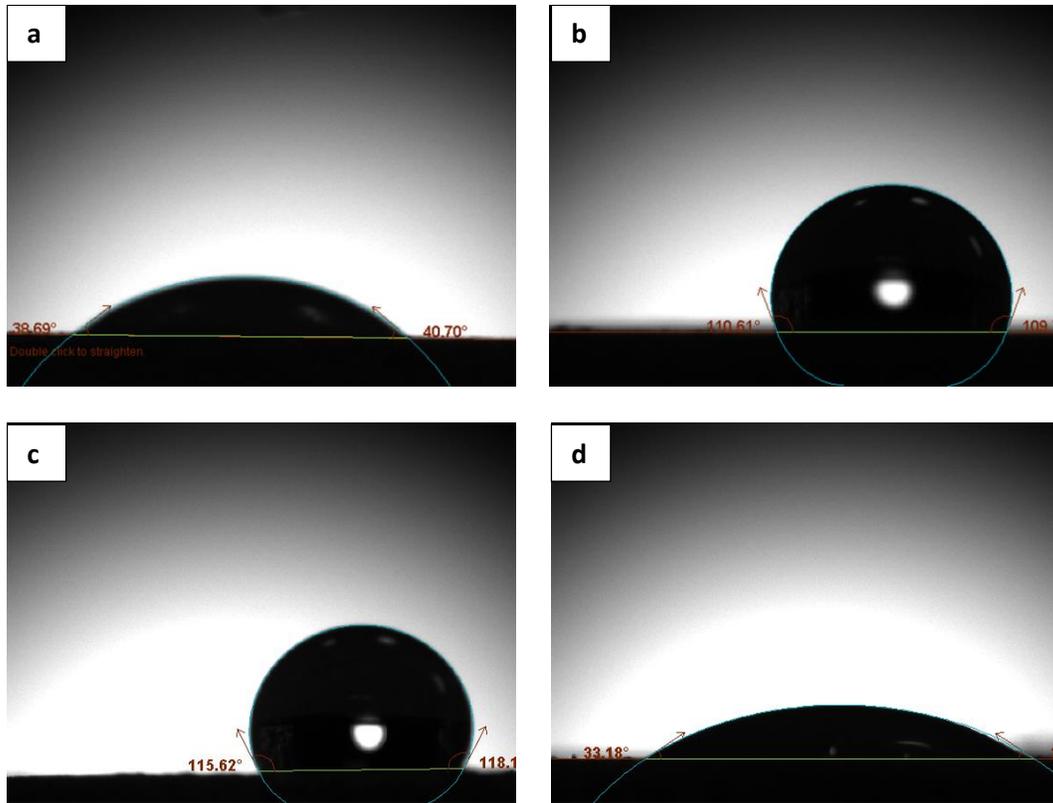


Figure 12: Contact angle of: a) Indianan limestone only b) Indiana limestone aged in crude oil c) Indianan limestone treated with seawater for one day d) Indiana limestone treated with MCM-41 suspension for 1 day

3.3.3 Responsive System

High salinity and temperature are the main challenges encountered in the oil reservoir, which challenge the deployment of surfactants and cause the systems to form waxy like inactive materials that may plug the pore spaces making it difficult to produce oil.^{21,42}

There is abundance of ions in underground waters due to the dissolution of the solid surfaces when they come in contact with water. The presence of ions can be leveraged as a trigger to optimize the slow release of surfactants. As we showed previously,¹⁴ the surfactant is only released in the presence of the ions in saline water. Here, we extend the study by showing how the wettability behaves when the particles

are suspended in deionized water for one day. As shown clearly in **Fig. 13**, the contact angle reduction is greatest when the particles are suspended in SW. The best performance of all the cases is for MCM-41 containing CTAB and suspended in SW. This could be understood by the fact that the ions in the seawater, more specifically the positive ions such as Ca^{2+} , drive the release of CTAB molecules through an ion exchange mechanism.

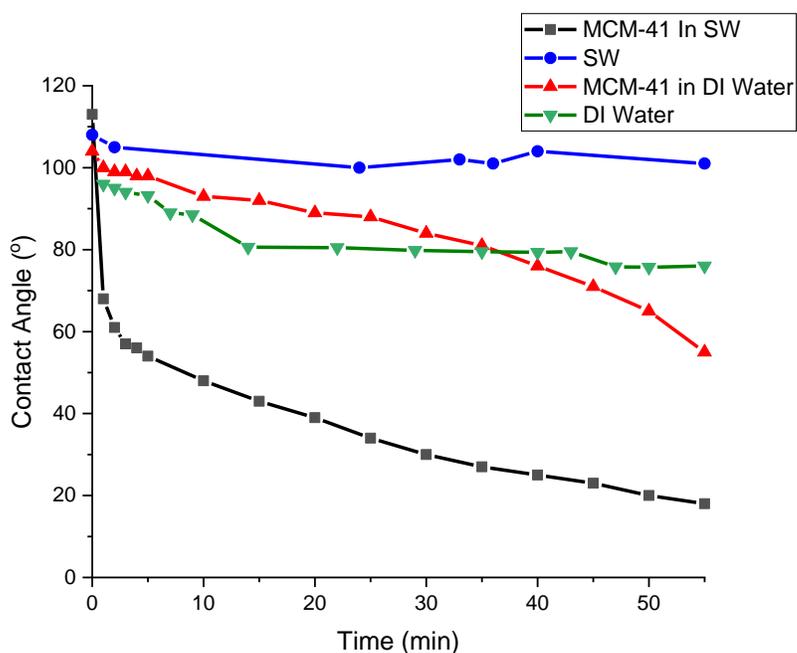


Figure 13: Contact angle comparison when the particles are suspended in SW and DI water

3.3.4 Interfacial tension study

Surfactants play a major role in lowering the interfacial tension.¹⁷ It is essential to show that the encapsulated surfactant, through the slow release, would still lower the interfacial tension. The experiments were conducted utilizing a spinning drop tensiometer with dodecane as model oil. The surface tension of dodecane with seawater was 62 mN m^{-1} at room temperature. The critical micelle concentration

(CMC) for CTAB dissolved in synthetic seawater was 4.2 mg L^{-1} where the IFT is 0.4 mN m^{-1} as shown in **Fig. 14**.

As shown in **Fig. 15**, the MCM-41 suspension results in ultralow interfacial tension that is three orders of magnitude lower than the oil-water IFT at a concentration of 0.175 mg ml^{-1} . At this concentration, there is about 0.012 mg ml^{-1} of CTAB released in solution, which is equivalent to the CMC concentration of CTAB. However, the reduction of the IFT is an order of magnitude lower than that for the surfactant molecules alone. Note that the value of the IFT for colloidal silica NPs functionalized with CTAB is orders of magnitude higher than what we obtained with the MCM-41 particles.^{43,44} We suggest that the synergistic effect is due to the slow and sustained release of surfactant molecules that minimizes the formation of bilayers and micelles that prevent normally adsorption at the oil-water interface and lower the efficiency.

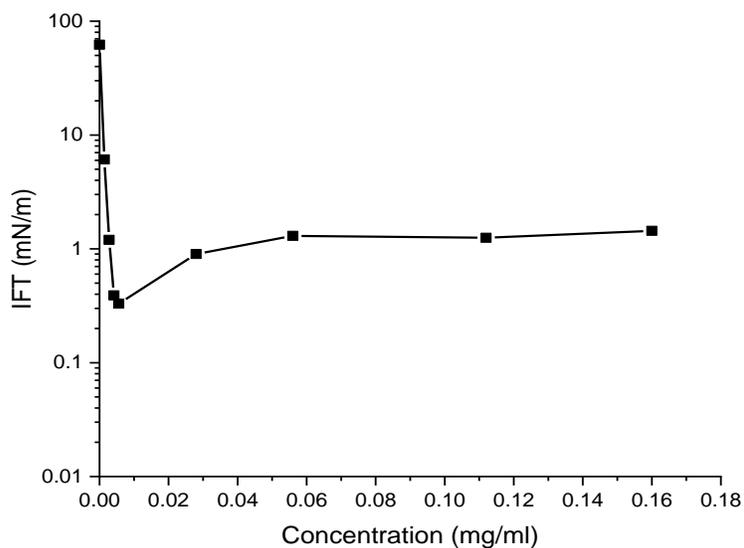


Figure 14: IFT for CTAB in seawater determines the CMC concentration at 4.2 mg/L

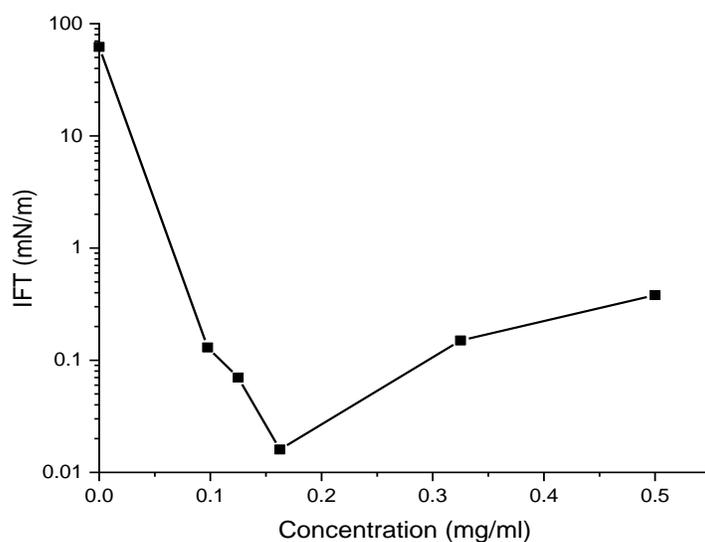


Figure 15: IFT measurements for the nano capsules at different concentration of MCM-41 particles.

To investigate the main drive for achieving low interfacial tension, the surfactant was extracted completely from the MCM-41 particles using ammonium nitrate.⁴⁵ As shown in **Fig. 16**, the IFT for surfactant-free MCM-41 is higher compared to the surfactant containing MCM-41 by one order of magnitude at 0.5 mg ml^{-1} suggesting that the presence of encapsulated surfactant is critical. In fact, without the surfactants, the silica NPs are hydrophilic and do not adsorb at the oil-water interface. The release of the surfactant molecules resulted in improving the interfacial properties of the MCM-41, and thus achieving lower IFT in comparison to the MCM-41 particles after removal of the surfactant molecules.

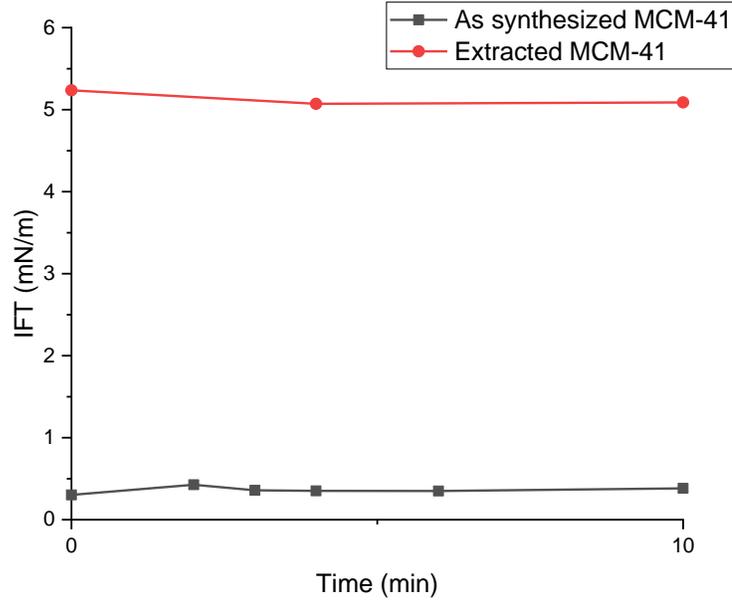


Figure 16: Comparison of the IFT between surfactant free MCM-41 and MCM-41 encapsulating surfactant

Adsorption to the oil-water interface facilitates the reduction of the interfacial energy. To show this kinetically, Bizmark et al. proposed the following equation that relates the dynamic interfacial tension with the interfacial energy:⁴⁶

$$\gamma = \gamma_o - 2N_A\Delta EC_o\sqrt{\frac{Dt}{\pi}} \quad 2$$

where γ is the interfacial tension and γ_o is the pristine interfacial tension both in (mN m^{-1}), N_A is Avogadro's number ($6.022 \times 10^{23} \text{ mol}^{-1}$), ΔE is the surface energy (J), C_o is the concentration of nanoparticles ($\text{mole } m^{-3}$) and D and t is the diffusion coefficient ($m^2 \text{ s}^{-1}$) and time (s), respectfully. A plot of the dynamic interfacial tension and the square root of time gives an indication of the dynamic adsorption of the nanoparticles at the interface.

As shown in **Fig. 17**, the plot of the IFT versus the square root of time gives a linear relationship that extends for a longer time scale compared to that when there is a high concentration of the nanoparticles. When there is a high concentration of particles, there is also a large amount of surfactant in the solution which can form a bilayer that makes the particles partially hydrophilic preventing their adsorption to the oil-water interface. Secondly, the particle-particle interaction may result in aggregation and screening of the surface potential which makes them less favorable to adsorb to the interface. On the other hand, less concentration of the nanoparticles means that there is less amount of surfactant which prevents forming a bilayer and the particles will remain hydrophobic favoring adsorption to the oil-water interface. A comparison of the surface energy between two concentrations and the surfactant-free MCM-41 is given in **Table 1** which agrees with the presented data from the IFT in which lower interfacial energy is achieved with encapsulated CTAB MCM-41 particles.

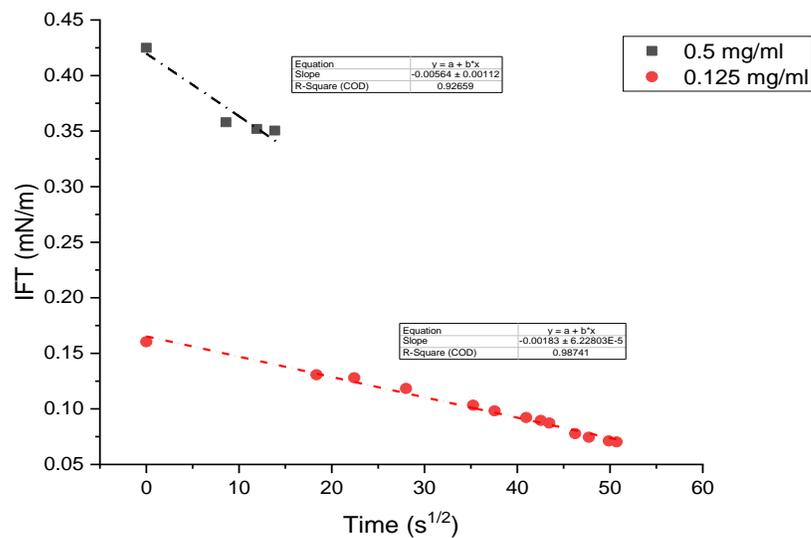


Figure 17: The interfacial tension measurements as an indirect indication of the adsorption kinetics of the framework onto the interface

Table 1: Comparison of the surface energy between different concentrations and systems

Concentration (mg/ml)	0.125	0.5	0.5 extracted
Surface Energy 10 ¹⁸ (J)	2.55	3.19	23.20

The thermal stability of the particles at high-temperature is a critical requirement. We have shown previously that even at high temperatures, the particles release surfactant molecules. We tested the IFT at increasing temperature and found that the capsules respond positively to heating where the interfacial tension decreases further from 0.5 mN m⁻¹ at 25 °C to 0.25 mN m⁻¹ at 80 °C (**Fig. 18**). The decrease of IFT in response to temperature could be due to that a) more surfactant is released from the particles and adsorb to the oil-water interface and b) the viscosity of the solution is lowered which also enhances diffusion.

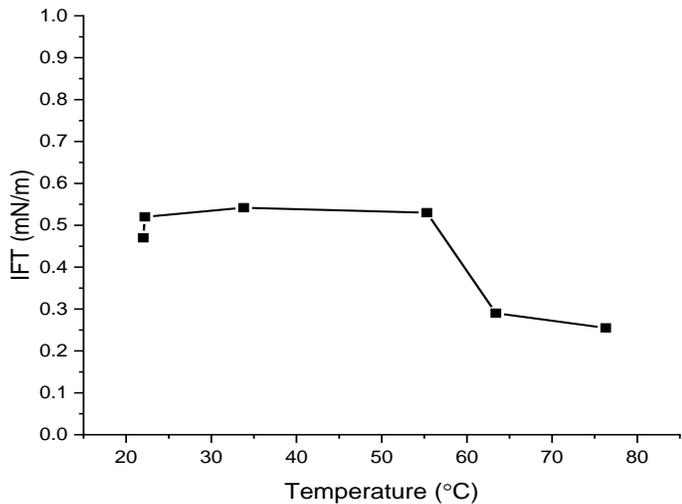


Figure 18: The IFT of the nanosized capsules decreases responds favorably to the increase in temperature

Fundamentally, the above two reasons could be physically seen from the Stokes-Einstein equation

$$D = \frac{K_b T}{6\pi\mu a} \tag{3}$$

where K_b : is Boltzmann constant ($1.38 \times 10^{-23} \text{ J K}^{-1}$), T is the temperature in Kelvin, μ is the viscosity (Pa s) and a is the radius of the molecule. Hence, as the temperature increases, the diffusion of surfactant from the mesopores is enhanced. Moreover, it can also be seen that the higher adsorption coefficient results in lower interfacial energy as shown in equation 3.

The second possible explanation is the decrease in viscosity. However, Eyring in 1941 derived an equation for the viscosity of liquids using the statistical mechanic approach.⁴⁷ The viscosity in his model of the molecules being in a cage is given by:

$$\mu = \frac{N_A h}{V} e^{\frac{\Delta F^*}{RT}} \tag{4}$$

where h is Planck constant ($6.626 \times 10^{-34} \text{ m}^2 \text{ kg s}^{-1}$), V is the volume (m^3), R is the gas constant $8.134 \text{ (J K}^{-1} \text{ mol}^{-1})$, and ΔF^* (J mol^{-1}) is the free energy of activation. It can be readily seen that the dependence of the viscosity in T when it increases from 298 K to 353 K is minimal and results in a change of less 1% in the viscosity. Hence, viscosity does not appear to play a major role in the decrease of IFT compared to the improvement in diffusion at higher temperatures.

Conclusion

In summary, we demonstrate a system for controlled delivery of surfactant based on CTAB encapsulated into mesoporous silica for efficient wettability alteration and to achieve ultralow interfacial tension. The surfactant molecules are used as templates and are incorporated into the mesopores of the resulting hexagonal silica particles of about 50 nm in diameter. The release of the surfactant was assessed by suspending the particles in both DI and high salinity water. The system shows a slow release profile in which only 50% of the surfactant is released within 10 days. Upon release glass or calcite treated surfaces transform from hydrophobic to hydrophilic. Importantly, the results indicate that the nanosized particles release their cargo of surfactants in the presence of the ions. The particles were able to reduce the interfacial tension three orders of magnitude at a concentration of 0.15 mg ml^{-1} . Finally, the particles respond favorably to increases in temperature with the interfacial tension decreasing from 0.5 mN m^{-1} at $25 \text{ }^\circ\text{C}$ to 0.25 mN m^{-1} at $80 \text{ }^\circ\text{C}$.

Acknowledgment

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CHAPTER 4
ENCAPSULATION OF ANIONIC SURFACTANTS: SIZE CONTROL, SLOW
RELEASE AND POTENTIAL USE FOR ENHANCED OIL RECOVERY
APPLICATIONS

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Abstract

Surfactant flooding has recently received widespread attention for Chemical Enhanced Oil Recovery (cEOR) changing the wettability of the rock and reducing the capillary forces that hinder the oil production. However, surfactant loss and adsorption on reservoir minerals are major challenges. This paper presents a new approach to encapsulate anionic surfactants into nanosized hollow-spherical silica particles which slowly release their cargo in high salinity water normally encountered in oil field applications. The applicability of the particles to be utilized for cEOR applications is assessed by studying the effectiveness of the particles to alter the wettability of hydrophobic surfaces. Moreover, the reduction of the interfacial tension of the

nanocarriers-brine-oil system is explored. The data reveal that different release profiles are present based on the size of the carrier. In addition, our studies show that the wettability alteration happens as a result of the release of surfactant from the porous nanocarriers. The interfacial tension of the oil-brine system was reduced by one order of magnitude when the nanocarriers were introduced into the solution.

4.1 Introduction

Surfactant injection has been extensively explored as one of the most efficient approaches for Chemical Enhanced Oil Recovery (cEOR). This method has a strong potential to reduce interfacial tension (IFT) and alter the wettability of hydrophobic surfaces to more hydrophilic to enhance oil recovery.¹⁻⁵ However, adsorption is a key limitation of utilizing surfactants, which requires injection a substantially larger amount from that needed. The addition of sacrificial chemicals to lower the adsorption has been explored. However, this is cost-intensive for the oil and gas industry.^{6,7} To overcome this limitation, the concept of the controlled, slow-release of surfactant molecules has emerged as one of the promising solutions for EOR.

Encapsulating surfactants into a compatible scaffold is, therefore, an attractive concept for EOR applications. Mesoporous materials represent a flexible platform that could be utilized to encapsulate surfactants. Since their discovery, mesoporous materials have attracted widespread interest in many applications such as drug delivery and biosensing,⁸⁻¹⁰ water treatment,^{11,12} catalysis^{13,14} and protective coatings.¹⁵ Among mesoporous materials, silica-based mesoporous materials are promising due to their stability and versatility.

Despite their widespread use, mesoporous materials have not been investigated for hydrocarbon recovery applications. Flávio et al.¹⁶ proposed utilizing a class of mesoporous materials (SBA-15) to control the delivery of surfactant. They utilized a nonionic surfactant that binds to the surface of the particles and slowly desorbs into the oil-water interface to lower the interfacial tension. However, in their study, the surfactant was physically adsorbed onto the particle surface, which due to the weak interaction between the surfactant and the silica surface can dissociate easily and suffer from the same issues as the neat surfactant injected directly into the reservoir.

Recently, our group demonstrated in a preliminary study¹⁷ that MCM-41 nanoparticles (below 100 nm) offer an effective platform for controlling the release of cationic surfactants from the mesoporous particles. However, one disadvantage of utilizing MCM-41 is its inability to host anionic molecules required to encapsulate anionic surfactants. A large amount of research work has been devoted to using cationic and nonionic surfactants to prepare mesoporous silica nanoparticles.¹⁸⁻²³ However, very limited information is available on synthesizing porous silica nanoparticles utilizing anionic surfactant.

Anionic surfactants could potentially enhance oil recovery by wettability alteration and reducing interfacial tension.²⁴ Anionic surfactants can tolerate high temperature and high ionic concentration environment both of which are associated with oil reservoirs. However, their adsorption to reservoir minerals remains the predominant challenge, which adds significantly to the cost.^{25,26} In addition, it can produce an unstable slug.²⁷

DOWFAX[®] is an anionic surfactant (**Figure S1**) that contains two sulfonated phenyl groups and has been studied for subsurface remediation activities. Furthermore, it has been investigated for environmental utilization such as enhancing contamination solubilization.^{28,29} Due to its sulfonate group, it is stable in the presence of calcium ions up to 0.1 M.³⁰ It has also received attention for EOR application starting in the 1970s as it displayed effectiveness in enhancing oil recovery and stability in the presence of monovalent and divalent ions.³¹ However, no previous attempts were made to encapsulate the surfactant for slow and controlled release.

In this paper we demonstrate a platform for the slow and controlled release of DOWFAX based on sub-100 nm hollow sphere-like silica nanoparticles. Surfactant release is accomplished due to the abundance of ions in oil field water which leads to a reverse ion exchange process. We study the release of DOWFAX in high temperature and high ionic strength solution, which mimics the reservoir conditions. To demonstrate their applicability of the new platform for EOR application, we further investigate the mechanism of altering surface wettability and the reduction of the interfacial tension using the encapsulated DOWFAX.

4.2 Experimental Section

4.2.1 Materials

DOWFAX[®] was purchased from Dow Chemicals Co. The average molecular weight is 576 and has 45% active ingredient with a density of $\sim 1.15 \text{ g ml}^{-1}$. The DOWFAX was used as templating material to synthesize the nanoparticles. Tetraethyl orthosilicate (TEOS) and (3-aminopropyl) triethoxysilane (APTES) were purchased from Sigma Aldrich and used. Sodium Chloride (NaCl), Calcium Chloride Dihydrate

(CaCl₂·2H₂O), Magnesium Chloride Hexahydrate (MgCl₂·6H₂O), Sodium Sulfate (Na₂SO₄) and Sodium Bicarbonate (NaHCO₃) were purchased Sigma Aldrich. Silicon oil and dodecane were used for the contact angle and interfacial tension measurements.

In order to mimic oil field brine, we utilized the brine composition proposed by Amr and coworkers.³² The preparation was carried out in a 1L volumetric flask. The amount of salts shown in **Table 1** were dissolved in 1 L of 18.2 MQ water, stirred and mixed at 40 °C.

Table 1: Salt amount used in the preparation of 1 L synthetic seawater

Compound	NaCl	CaCl ₂ ·2H ₂ O	MgCl ₂ ·6H ₂ O	Na ₂ SO ₄	NaHCO ₃
mass (g)	41.04	2.384	17.645	6.343	0.165

4.2.2 Synthesis of DOWFAX Capsules

A modified procedure described previously by Han and coworkers was used.³³ Briefly, DOWFAX was dissolved in a mixture of 100 ml 18.2 MQ water and 10 ml Ethanol. Then, the temperature was increased to 80 °C. After that, 2.4 ml of TEOS and 0.3 ml APTES was added dropwise to the mixture. In order to tune the size of the particles and the amount of DOWFAX different experimental parameters including stirring time, temperature and different molar ratios of DOWFAX, APTES and TEOS were experimented.

4.2.3 Characterization

Scanning Electron Microscopy (SEM) and Transition Electron Microscopy (TEM) images were obtained using a Mira Tescan and Tecnai T12, respectively.

Thermal Gravimetric Analysis (TGA) was obtained using Q500 TA instruments thermal analyzer. Fourier Transform Infrared (FT-IR) spectra were obtained on the Bruker Vertex V80V Vacuum FTIR System. UV-Vis spectra used to quantify the surfactant release were acquired by Molecular Devices. Contact angle measurements were performed utilizing Contact Angle Tester by Biolin Scientific.

4.2.4 Release Experiments

The surfactant release was measured by dissolving 10 mg of the solid in 20 ml of seawater and measuring the concentration of the surfactant released by UV-Vis spectroscopy. Detailed information is provided in the supporting information.

4.2.5 Wettability Alteration Experiments

Wettability alteration experiments were performed to evaluate the effectiveness of the system in transforming an oil-wet to preferential water-wet surface. It is well established that oil recovery increases with increasing the hydrophilicity of the oil reservoir.³⁴ To determine the degree of alteration, contact angle measurements were used.³⁵ Silane oil was used to coat glass slides to form a highly stable hydrophobic surface.³⁶ The glass slides were immersed in the oil bath and aged in a vacuum oven at 80 °C for 4 days. After that, the slides were washed with DI water and dried at 80 °C in a vacuum oven for 2 days. We utilized the sessile drop technique to determine the wettability of the glass surfaces. A drop of the solution is placed on the glass slide and then the contact angle was recorded for a period of 55 minutes. The degree at which the drop is spreading over the surface is utilized to indicate the efficiency of the system in altering the wettability.

4.2.6 Interfacial Tension Measurements

The interfacial tension is a useful indication of how the capillary forces between oil and water change in the presence of active material. The capillary number is given by the following equation:

$$N_c = \frac{\mu v}{\sigma_{ow}} \quad 1$$

Where N_c is the capillary number, μ and v are the viscosity and speed of the displacing fluid, respectively and σ_{ow} is the oil-water interfacial tension.

As indicated by the equation, there are two possible ways that can increase the capillary number: increasing the viscosity or lowering the interfacial tension.

Reducing the interfacial tension by adding surfactants could result in overcoming the capillary forces, which hinder oil production, thereby, improving the oil recovery.³²

A spinning drop tensiometer (SDT) by Kruss was used to measure interfacial tension. The temperature for the experiments ranges from 25 °C to 80 °C to simulate the reservoir conditions. Dodecane is used as the light phase and sea water as the heavy phase. The respective densities are 0.75 g ml⁻¹ 0.99 g ml⁻¹.

4.3 Results and Discussion

4.3.1 Optimization of the Nanocapsules Size

DOWFAX is an anionic surfactant containing two sulfonated phenyl groups. As stated previously, this surfactant has been used for cleaning organic contamination from the soil and is stable at a high concentration of divalent ions, which is a crucial requirement for applications in enhanced oil recovery. It was previously tested for

enhanced oil recovery using Berea sandstone rocks and shown to increase the oil recovery by 25%.³¹

In the first attempt to encapsulate DOWFAX, where the mixture was stirred only for two hours and then aged for 48 hours, the resultant capsules, D_1 exhibited irregular shape with a size larger than 200 nm as revealed by TEM (**Fig. 1a**). To investigate the effects of stirring on shape and size of the particles, another synthesis was carried out with similar molar ratios to above but maintaining a stirring speed of 100 RPM for 48 hours. While the shape of the particle became mostly spherical (D_2), the size remained larger than 200 nm as shown in (**Fig. 1b**). For practical applications, the size of the particles is important. For example, to use nanoparticles for oil applications and be able to access the smaller pores, it is desirable to use particles that are less than 100 nm. Injection of large size particles in the oil reservoir, addition to accessibility issues, may eventually result in plugging the pores which of course will have a detrimental effect on oil recovery.³⁷ Therefore, further optimization to achieve sub-100 nm particles was necessary. The D_3 system with a formulation provided in **Table S1** results in particles with a size ranging from 50 nm to 200 nm as shown in (**Fig. 1c**). Moreover, the particles exhibit uniform spherical shape. Further optimization by controlling the molar ratio of reactants led to smaller size particles. The system described as D_4 shows sub-100 nm in size with a uniform spherical shape (**Fig. 1d**). The TEM images further reveal that the particles have a hollow-sphere like structure.

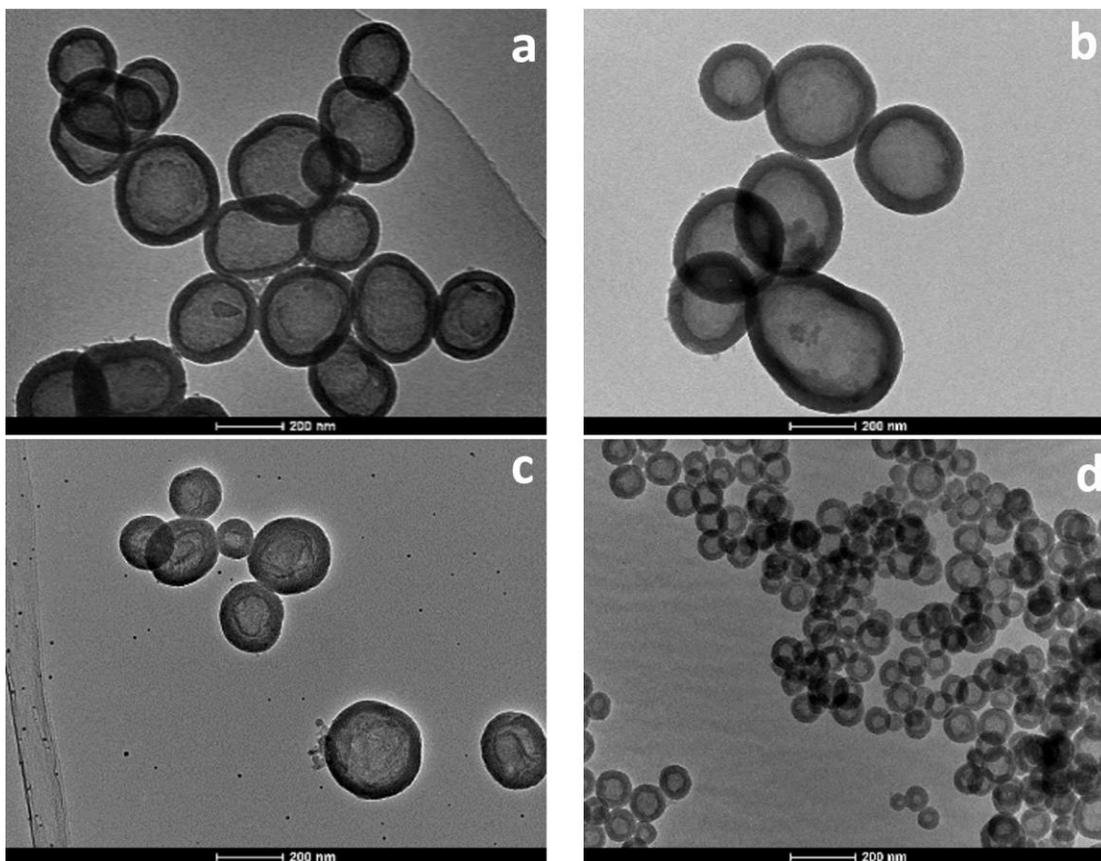


Figure 1: TEM images of the different synthesis routes. a:D_1, b:D_2, c:D_3 &d:D_4

Additionally, the size of the mesopores as determined by BET analysis is 4.5 nm. More importantly, the mesopores formed by templating around the surfactant molecules retaining the surfactant inside the pores rather than physical binding onto the surface. Optimizing the amount of surfactant used in the synthesis would minimize the excess surfactant molecules that binds to the surface. It is also clear that the size of the particles depends greatly on the molar ratio of TEOS, APTES, and DOWFAX. Moreover, the irregularity and the size of the synthesized nanoparticles depends on the nucleation process, which is also a function of the TEOS/APTES/Surfactant ratio. The presence of ethanol in the mixture slows the hydrolysis rate of TEOS and APTES,

which would result in a reaction that is kinetically controlled. On the other hand, APTES can act as a catalyst that accelerates the hydrolysis process which leads to larger size particles.³³ By controlling the particle size and further limiting the rate of nucleation by the stirring speed, we are able to produce sub-100 nm size capsules with DOWFAX encapsulated into the hollow core. One interesting consequence of the size control is the amount of DOWFAX encapsulated. As shown in **Fig. S2**, the amount of DOWFAX encapsulated in D_4 is 40 compared to 30% in D_1.

4.3.2 Slow Release of DOWFAX

Surfactant flooding is challenged by the fact that for successful implementation, large quantities are needed to overcome adsorption, which leads to high cost.³⁶ A potential solution is slow release that makes the surfactant available deeper in the reservoir. The surfactant release profile of various systems in seawater is shown in **Fig. 2**. For the large particles, the release reaches 14 % even after a long period of time. In contrast, for the smaller size particles, the release is higher. The D_3 capsules show two distinct profiles. The first part, within the first five days, is a linear. It is followed by a slower increase in surfactant concentration until it levels at 25% after 20 days. D_4 also follows a similar profile and it plateaus at 18% within the first 10 days.

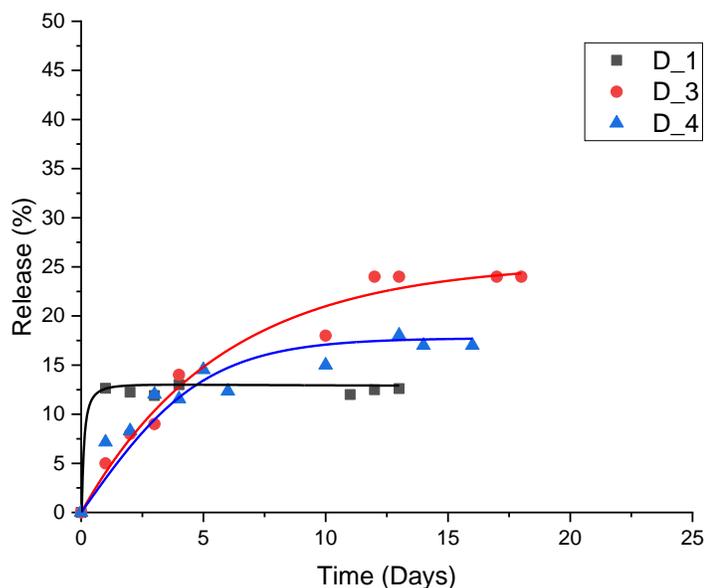


Figure 2: Release profile for DOWFAX from the different sized capsules

There are two possible explanations with regard to the different profiles. For the smaller particles the surface area is larger providing more contact and accessible sites with the ions in the seawater. Moreover, the dispersion of particles is enhanced with decreased size providing more interaction with the salts that are present in seawater, which in turn increases the reverse ion exchange rate between the surfactant molecules encapsulated in the host and the ions in the seawater.

The rate of release was also studied at an elevated temperature closer to the conditions, which are normally encountered in the reservoir. **Fig. 3** shows clearly that the release of the surfactant is enhanced at high temperatures. The amount of DOWFAX release is doubled compared to the release at room temperatures. This enhanced release is probably due to an increased rate of collisions of the particles as a result of the increase in temperature and/or weakening of the bonds between the SO_3^-

on the surfactant molecules and NH_2^+ on the host (due to the increased vibration as a result of increasing the temperature).

The slow-release profile is very essential for oil field applications.

Nanoparticles require months to travel from an injector to a producer. For example, It has been shown that fluorescent tracers injected in a water injector required 50 to 200 days to be recovered from a producer that is 500 m away.^{37,38} For the nanosized capsules only 40% of the surfactant is released within the first 20 days, followed by a much slower release rate suggesting that they can reach deep into the un-swept reservoir areas due to their slow release kinetics.

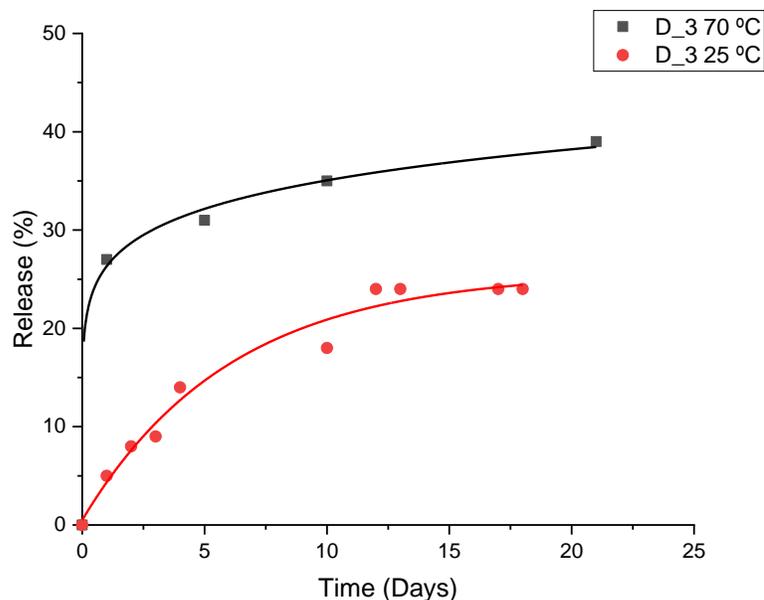


Figure 3: Release of DOWFAX from D_3 at high Temperatures

4.3.3 Wettability Alteration Performance

The tendency of a fluid to adhere to a solid surface in the presence of another immiscible fluid defines its wettability. It is a crucial property when evaluating multiphase flow in solid surfaces. It controls the distribution of oil and water in the

reservoir and, hence, has a great impact on oil recovery.³⁶ Surfaces with a contact angle above 90° are considered oil-wet while those less than 90° are water-wet. The change of the wettability from oil-wet to water-wet can significantly increase the capillary pressure as shown by Young-Laplace equation³⁹:

$$P_c = \frac{2\sigma_{ow}}{r} \cos(\theta_{ow}) \quad 2$$

where P_c is the the capillary pressure, σ_{ow} is interfacial tension between oil and water, θ_{ow} is the contact angle and r is the pore throat radius. The effectiveness of altering the wettability is shown in **Fig. 4**. When a drop of seawater is placed on the hydrophobic surface that is coated with oil, the contact angle remains constant. However, when D_3 was first hydrolyzed in seawater for 1 day and then a drop of the suspension was placed on the glass slide, the contact angle dropped linearly with time until it reached below 30° clearly demonstrating that the released surfactant molecules are effective in altering the surface wettability substantially.

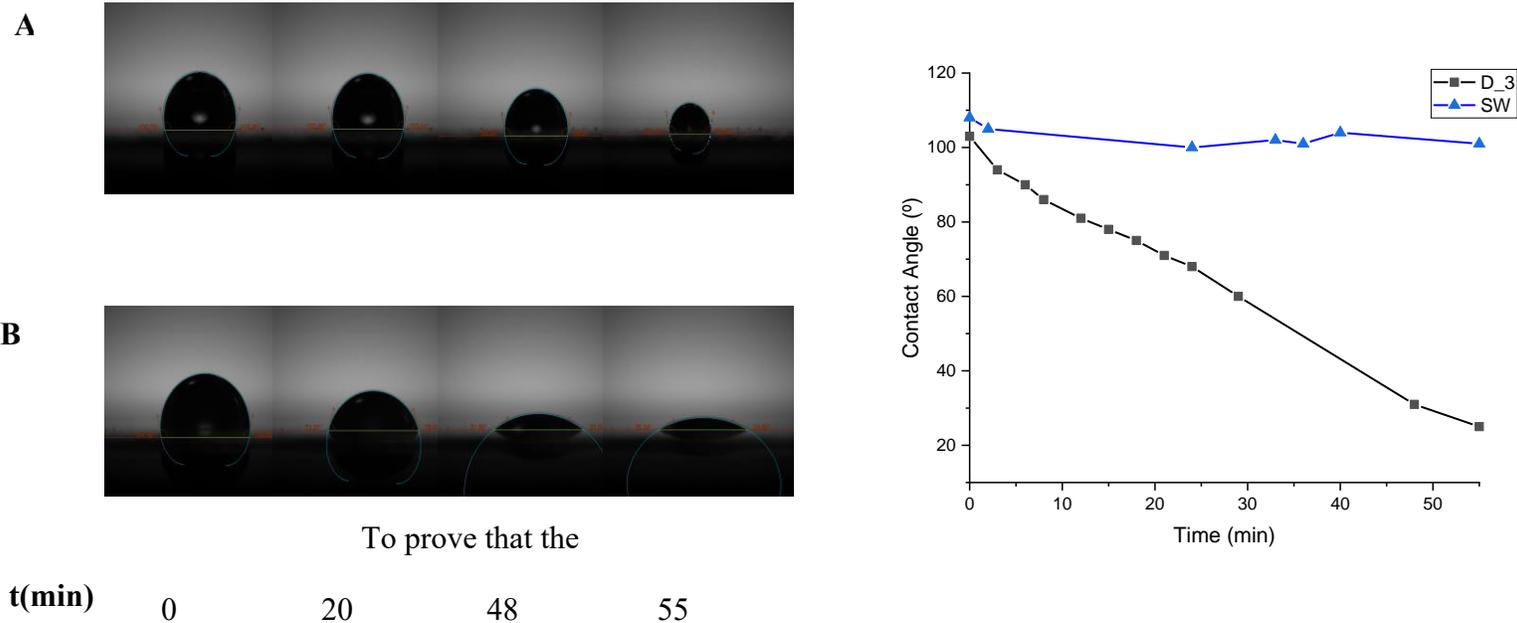


Figure 4: Contact Angle Measurements for Seawater and D_3 in Seawater. A is the contact angle of Seawater over 55 minutes and B is the contact angle of D_3 in Seawater

To prove that the mechanism for the wettability alteration is the slow release of surfactant, the capsules were tested after the DOWFAX molecules were removed from the system (D_3) by heating the powder under N₂ at 600 °C for 6 hours. The particles D_3 that have been first hydrolyzed for 1 day, the surfactant-free capsules, and the neat surfactant (0.15 mg ml⁻¹, which is the total concentration of the material encapsulated in 0.5 mg ml⁻¹ of D_3) are shown in **Fig. 5**. As can be seen the surfactant-free capsules showed no major alteration of wettability confirming that the released surfactant is responsible for the observed changes.

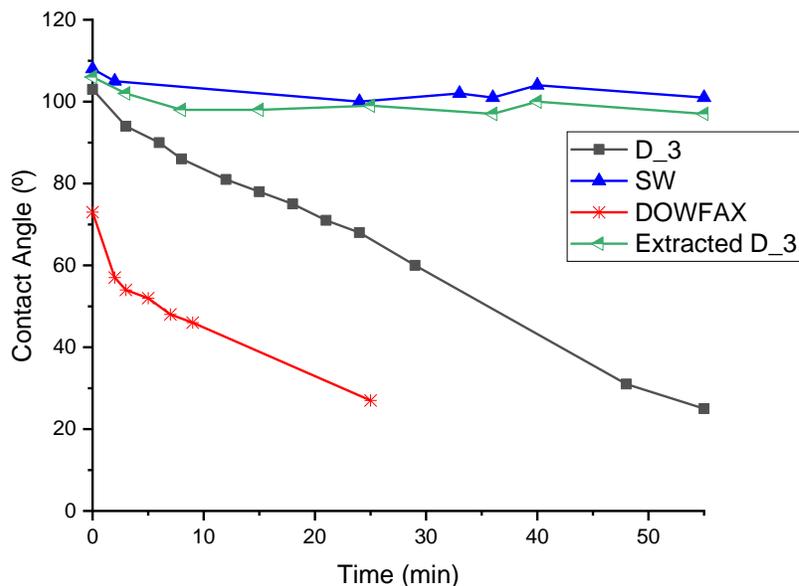


Figure 5: The contact angle shows the effectiveness of the slow release of surfactant to alter the wettability

The change in surface wettability utilizing an anionic surfactant is believed to be caused by the hydrophobic interactions between the surfactant and the oil layer coating the glass slide. It is assumed that one reason for the reduction in wettability is the formation of a bilayer of the surfactant with the hydrophilic part pointing upward. The anionic end of a water-soluble surfactant would end up facing toward the flow creating a zone of hydrophilicity. Due to the strong hydrophilic interactions, the surfactant will push and displace the oil that coats the glass surface. A similar mechanism was proposed by Nguyen et al. for nonionic surfactants.⁴⁰ However, in our system, there are two major interactions to consider. Since the neat silica nanoparticles are hydrophilic, they are not expected to interact strongly and displace the oil phase. Nevertheless, the nanoparticles could still exert a force on the surface of the oil phase creating high pressure and velocity potential zone that pushes the oil aside. Moreover,

the presence of the surfactant in the solution after it is released from the silica framework improves the hydrophobic interactions between the particles and the oil, which further enables a better sweep of oil. The proposed mechanism is shown schematically in **Fig. 6**. The large pressure gradient created and velocity potential in the r direction, the particles settle on the surface is also shown.

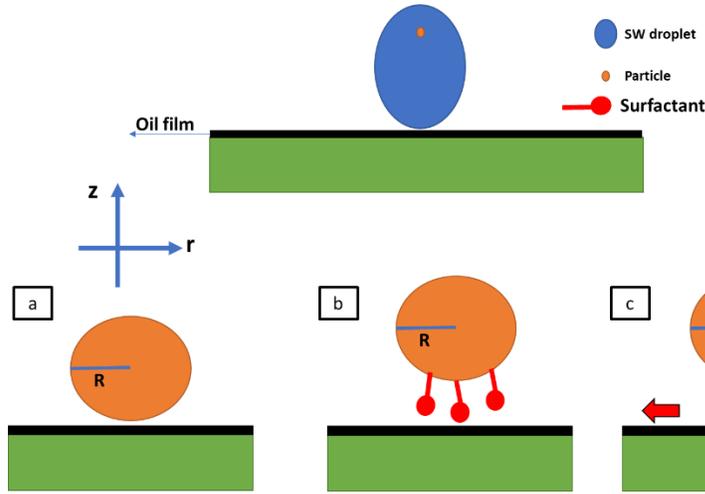


Figure 6: Schematic representation of the process of wettability alteration aided by the release of surfactant: a: nanoparticle free of surfactant changes the wettability due to the velocity gradient b: release of surfactant enhances the wettability alteration by pushing the oil in the r direction

The mass conservation of a particle settling on a surface with a nearly unidirectional flow is given by:

$$\frac{\partial V_z}{\partial Z} + \frac{1}{r} \frac{\partial}{\partial r} (rV_r) = 0 \quad 3$$

Where V_z and V_r are the velocities in the z and r direction. Utilizing scaling proposed by Koch⁴¹ to nondimensionalize the equation:

$$\bar{z} = \frac{z}{R\varepsilon} \quad 4$$

$$\bar{r} = \frac{r}{R\varepsilon^{\frac{1}{2}}} \quad 5$$

where R is the radius of the particle and ε is a separation parameter that is small and is used for the scaling of the separation between the particle in the surface. It is found that the characteristic velocities in the z and r directions are given by:

$$\bar{V}_z = \frac{V_z}{V} \quad 6$$

$$\bar{V}_r = \frac{V_r}{V^*} \quad 7$$

where V is the settling velocity of a spherical particle, V^* is a characteristic velocity to be found by the balance between the z and r coordinates in the mass conservation. The bar indicates nondimensional quantity. Substituting back in equation 3 yields the first significant result which is:

$$V^* = \frac{V}{\varepsilon^{\frac{1}{2}}} \quad 8$$

From the above $V_r \gg V_z$, which is consistent with the idea that the oil coating the surface is forced in the r direction. Solving the Navier-Stokes equation in cylindrical coordinates utilizing the scaling for the velocities shown earlier, the non-dimensional pressure is obtained:

$$\bar{P} = \frac{3}{(1 + 0.5r^2)^2} \quad 9$$

At the origin $z=r=0$, the dimensional pressure is given by:

$$P = \frac{3\mu v}{R\varepsilon^2}$$

10

And assuming for simplicity that the velocity, which is in the order of 10^{-6} m s^{-1} in the reservoir cancels with the small separation parameter ε , the pressure then scales with the inverse of the radius of the particle. That is, the smaller the particle, the higher the pressure generated at the point, where it settles. However, **Fig. 5** shows that, when the surfactant is extracted from the particles, the change in contact angle is not significant. Therefore, another interaction energy must be present to facilitate the alteration of wettability and consistent with that the release of the surfactant facilitates the alteration through the hydrophobic interaction with oil.

To further investigate the surface of the glass slides after treatment with D_3, we used FTIR spectroscopy. The glass slides were soaked in a solution of D_3 in seawater for 2 hours. After that, the glass was dried in a vacuum oven at $80 \text{ }^\circ\text{C}$ for 3 days. The results are shown in **Fig. 7**. The peak intensity of CH_2 and CH_3 groups at $\sim 2960 \text{ cm}^{-1}$ is significantly reduced. Hence, the contact angle measurements combined with the IFT observation show the robustness of the nanocapsules in altering the wettability.

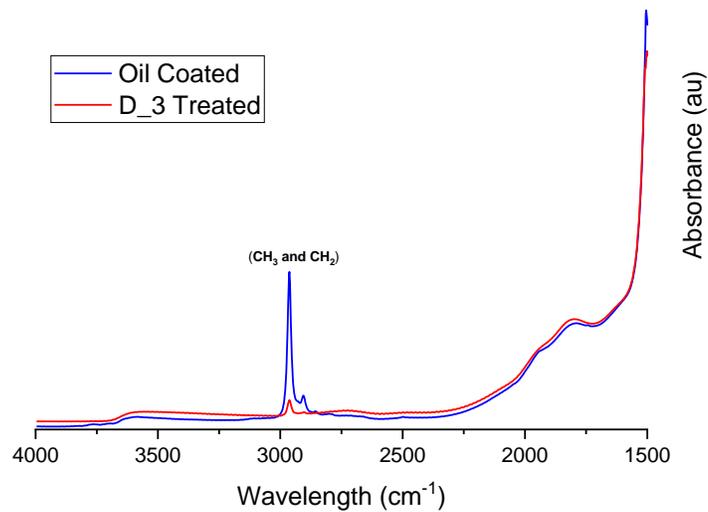


Figure 7: Effect of treating hydrophobic glass sheet with D_3 in seawater

4.3.4 Interfacial Tension Experiment

Another important indication of the applicability of a system to enhance oil recovery is the reduction of the interfacial tension between oil and water. Low IFT has been reported to result in achieving a higher ultimate oil recovery compared with brine.³⁴ To test the effectiveness of the DOWFAX capsules, several IFT experiments have been conducted. to show their performance over days and at elevated temperatures. First, the critical micelle concentration (CMC) of DOWFAX in seawater was determined. As seen in **Fig. 8** the CMC is 0.126 mg ml^{-1} above which the IFT increased slightly and remained constant at 1.29 mN m^{-1} . Note that the maximum concentration available of surfactant in the systems tested is 0.15 mg ml^{-1} which suggests that the concentration of the surfactant in these experiments will be near CMC but not much above it. In addition, the surface tension of the seawater-dodecane system stabilizes at 62 mN m^{-1} as shown in **Fig 9**.

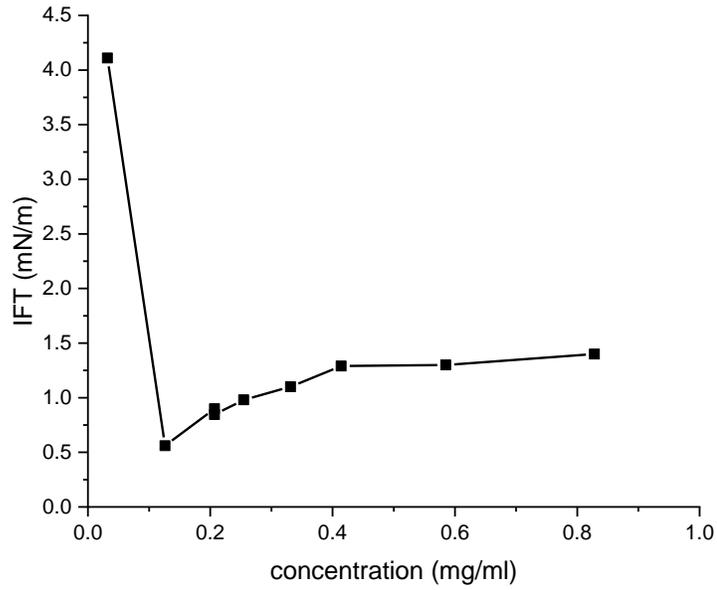


Figure 8. The CMC Determination of DOWFAX Surfactant in Synthetic Seawater

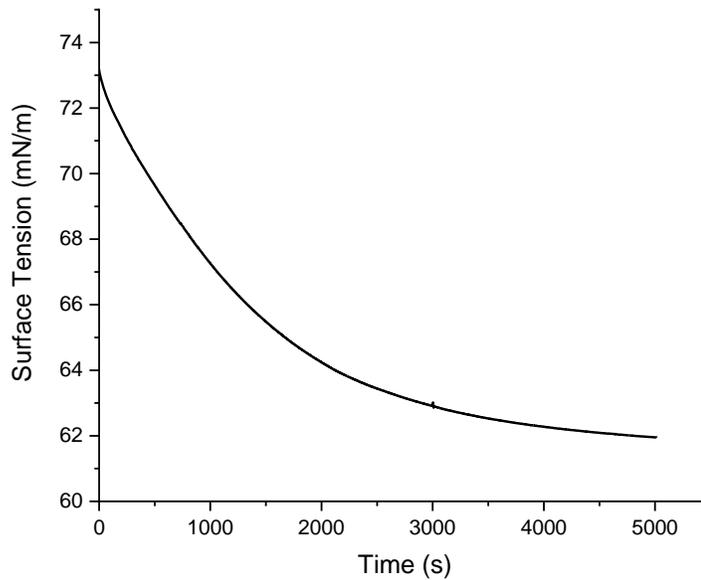


Figure 9: The surface tension between Synthetic Seawater and Dodecane

As stated previously, the effect of reducing the interfacial tension on the capillary number is expressed by the following equation $N_c = \frac{\mu v}{\sigma}$. Experimental studies concluded that the oil saturation decreases, when the capillary number

increases.⁴² The interfacial tension of dodecane/seawater in the presence of 0.5 mg ml⁻¹ D_3 previously immersed in seawater for various times is shown in **Fig. 10**.

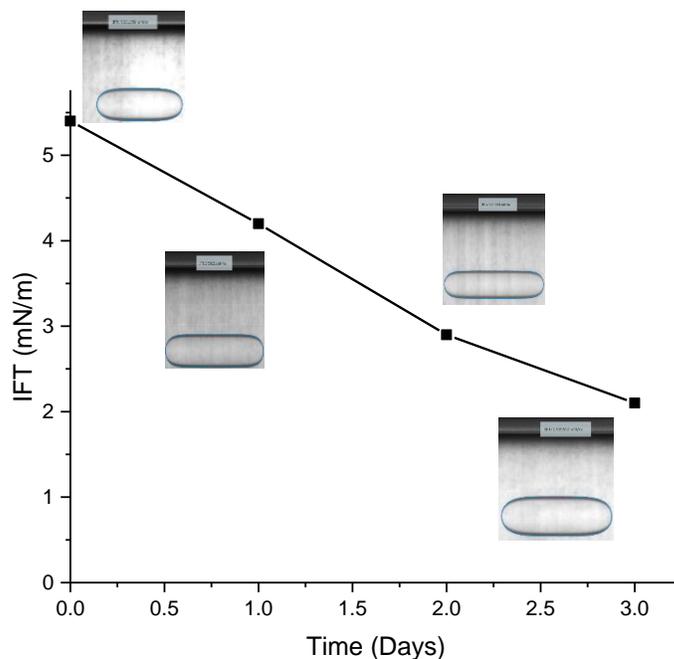


Figure 10: IFT Results of D_3 for 3 Days

After 3 days of immersion in seawater and surfactant release the nanosized capsules are able to reduce the interfacial tension of dodecane/seawater mixture 10 times. Moreover, as a result of the slow release of surfactant, it is shown that the IFT is a function of time achieving lower IFT as more surfactant is released from the nanocapsules. The system is expected to be functional for a long time when deployed in an oil reservoir where it takes nanoparticles around a month to travel from an injector to a producer.³⁷ The previous experiments show that the particles would still be functional with time and that it only releases 35% of the surfactant encapsulated.

Oil reservoir temperatures could be as high as 100-120 °C.⁴³ Therefore, it is crucial to test the performance of the system at elevated temperatures. **Fig. 11** shows

clearly that the IFT is reduced at elevated temperatures. Similarly, to **Fig. 8**, they form a V-shaped plot as a result of having more surfactant present in the solution. The diffusion is a process that is enhanced at elevated temperatures as seen by the Stokes-Einstein equation:

$$D = \frac{K_b T}{6\pi\mu R} \quad 11$$

where is K_b Boltzmann constant ($1.38 \times 10^{-23} \text{ J K}^{-1}$), T is the temperature in Kelvin, R is the radius of the molecule or the particle if it is small enough to follow random motion. Therefore, higher temperatures result in increased release of surfactant from the pores of the particles. This result indicates that the capsules and the surfactant are stable and the slow release of the surfactant leads to a gradual decrease of the IFT at the conditions encountered in oil reservoir.

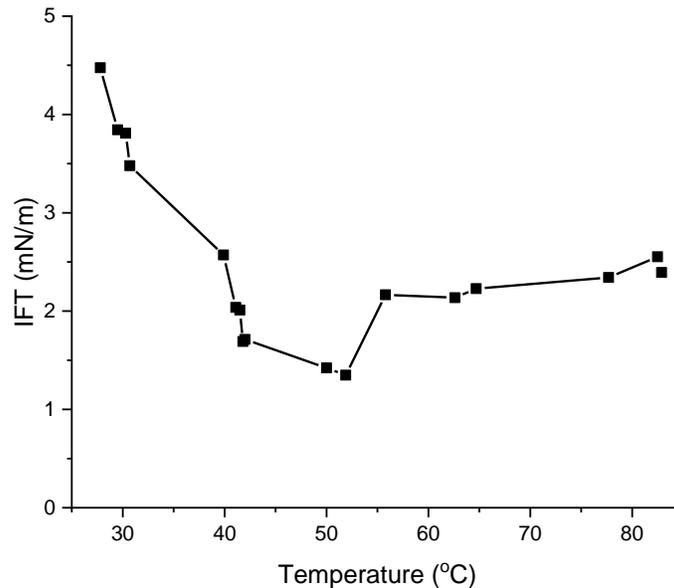


Figure 11: The IFT Results of D_3 at high temperatures showing improved performance of the nanocapsules as the temperature increases

Conclusions

A new platform for slow release of an anionic surfactant (e.g. DOWFAX) has been demonstrated. The system is based on surfactant molecules incorporated into sub-100 nm hollow sphere-like silica nanoparticles with mesoporous shell. The size of the nanocapsules was optimized by varying experimental parameters that affect the nucleation and growth during the synthesis reaction. The applicability of the system for hydrocarbon recovery applications was demonstrated in both room and elevated temperatures in seawater medium. Moreover, the ability of the particles to alter the wettability of hydrophobic surfaces was tested and showed that the release of the surfactant alters an oil-wet surface to a more favorable water-wet. Finally, the interfacial tension between dodecane/seawater was lowered by an order of magnitude by incorporating the nanocapsules in the seawater.

Acknowledgment

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Supporting Information

Release Experiments

The release of the surfactant was determined utilizing Uv-Vis. The DOWFAX Surfactant gives a distinct peak at a wavelength of 230 nm. In one experiment, 10 mg of nanosized capsules were dissolved in 20 ml of synthetic seawater. The mixture was kept stirring at either room temperature or 70 °C in oil bath. The sample was then centrifuged and the supernatant was analyzed to determine the concentration of DOWFAX released in the bulk fluid. The concentration of DOWFAX is then determined by the following equation:

$$C_i \left(\frac{g}{ml} \right) = 5 \times 10^{-5} * Absorption \quad 1$$

C_i : Concentration and the subscript i refers to the concentration at time i . The maximum amount of DOWFAX that is encapsulated is then:

$$C_x \left(\frac{g}{ml} \right) = x \times \frac{m}{v} \quad 2$$

Where:

C_x : Concentration of DOWFAX encapsulated in the nanoparticles

x : Percentage of organic content determined by TGA

m : mass of nanoparticles dissolved in synthetic seawater

v : volume of synthetic seawater

Then the release percentage of DOWFAX is determined as follow:

$$Release(\%) = \frac{C_i}{C_x} \times 100$$

3

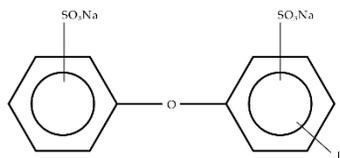


Figure S1. DOWFAX Surfactant general structure

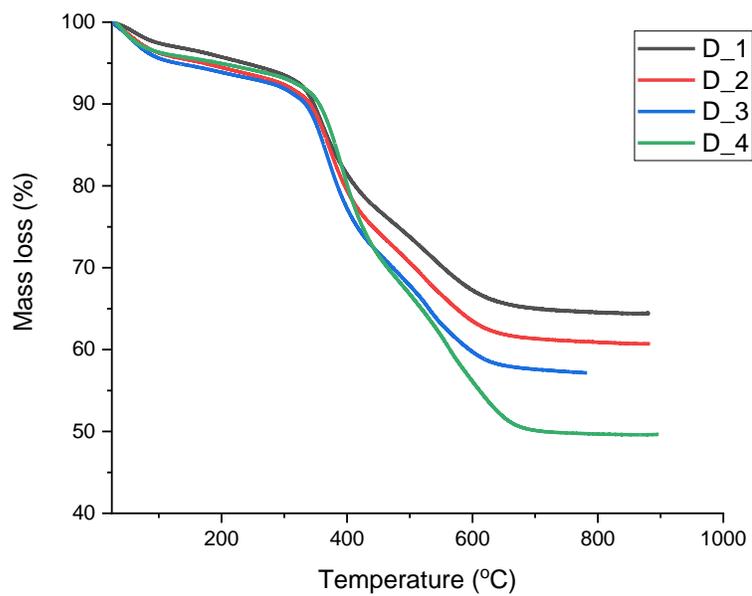


Figure S2.TGA of the different encapsulation reveal organic content dependence on the size of the particles

Table S1: DOWFAX capsules synthesis procedure and molar ratio of reactants

Recipe#	D_1	D_3	D_4
Molar Ratio (H ₂ O/ETOH/DOWFAX/APTES/TEOS)	833/25/1/0.7/2.5	926/29/1/0.3/1.3	1159/35.5/1/0.4/0.9
Stirring Speed (RPM)	0	300	400
Temperature (°C)	80	70	70(2hrs) 25 (22hrs)
Aging (Days)	1	2	1
Size (nm)	150-500	75-200	50-100
Shape	irregular	spherical	spherical
Organic content (%)	29	35	42