



Norwegian University of
Science and Technology

INJECTION OF SYNTHETIC PRODUCED WATER INTO POROUS MEDIA

A study of transport of dispersed components
through simulated reservoir packs

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To my brother who helped me achieve the impossible

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Abstract

Produced water(PW) contributes to the largest volume byproduct from the oil production industry. The presence of hazardous chemicals makes the handling of PW an important and costly operation. Methods such as discharge into the ocean, beneficial reuse, and re-injection into the well formation to maintain the well pressure and also to enhance the oil recovery are being practiced currently. Discharge into the ocean was the most preferable option until few years back. Increased concern about the environment caused formation of pollution control authorities all over the world which enacted stringent quality requirements prior to the discharge. This strict regulations caused the treatment of PW more costly forcing the companies to look for alternatives. In the recent years, the use of produced water as re-injection fluid has been increased due to both environmental and economical reasons. The transport mechanism and effects of different parameters need to be understood in order to design a suitable and economical treatment method. Numerous laboratory based experiments are conducted so far, mostly core flooding experiments. Still a clear image of the fate of the droplets inside the porous medium is missing. A real time observation of the porous medium during emulsion transport will give a better understanding about the transport mechanism. This is the main idea behind this project.

In this project, the validity of the deep bed filtration model was tested using a purpose built cell. The results obtained were agreeing to that observed in most of the core flooding experiments. Furthermore, the effect of different parameters on emulsion transport such as flow rate, ratio of droplet size to pore size, salinity, and the chemical composition of the dispersed phase. Model emulsions made of hexadecane, two crude oil distillate cuts having different densities were used to study the effect of different parameters. Finally, a more realistic study was done using an oil in water emulsion made of crude oil to study the same parameters. The analysis of inlet and outlet initial droplet size distribution along with the visual observation of the cell helped in understanding the flow mechanism and the effect of different parameters.

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Abbreviations

IFT = Interfacial tension
PW = Produced water
TOC = Total organic carbon
WGR = Water to Gas ratio
WOR = Water to Oil ratio

Introduction

This is the continuation of the specialization project done in Fall 2017, as a part of the curriculum. Therefore some part of the introduction and theory from the report written for the specialization project[1] is used in this report.

Produced water (PW) is the term used in oil industry to describe the waste water brought into the surface from the underground reservoir during the oil drilling process[2]. It contributes to the largest volume byproduct of oil exploration. Water can be present along with the hydrocarbon, sometimes associated with the oil or as a separate layer below the hydrocarbon reserve. The amount of water produced will increase as the well ages which results in a higher water to oil ratio (WOR). The recent estimated WOR is 4:1[3]. Handling this water is a big challenge and requires expensive treatment methods. The common method of handling PW is to discharge into the ocean. But this creates environmental issue due to the chemicals present in the PW which can cause chronic ecological harm[4]. Among the chemicals which are already present in PW or have been introduced during the production process, the residual oil content is one of the most important parameters[2]. The maximum oil content is restricted by the handling method. In case of disposal into the ocean, PW needs to meet the environmental regulation. In Norway the value is 30 mg per liter as per SFT (Norwegian pollution control authority)[5]. Therefore, the PW to be treated prior to disposal. The technologies selected for treatment will depend on whether the installation is onshore or offshore. For onshore, footprint is less critical and hence high footprint low energy technologies can be used [6].

The Figure 1.1* shows a typical offshore treatment unit. As mentioned already this process is expensive and energy consuming. The quality requirement is less stringent in case of re-injection into the oil well, which is an alternate handling method. Here the treatment methods largely depend on the nature of the well and it varies from well to well. An understanding of the reservoir and the transport of emulsion through the porous media, since hydrocarbons make an emulsion with the water, is inevitable to design a proper treatment method[5]. This makes a study of transport of emulsion through porous media and the different parameters affecting the transport important. The fact that the mechanism of emulsion transport is very difficult to capture creates a requirement for

*Figure taken from the article written by Vincenzo Piemonte, Associate Professor, University UCBM Rome (Italy) about produced water treatment

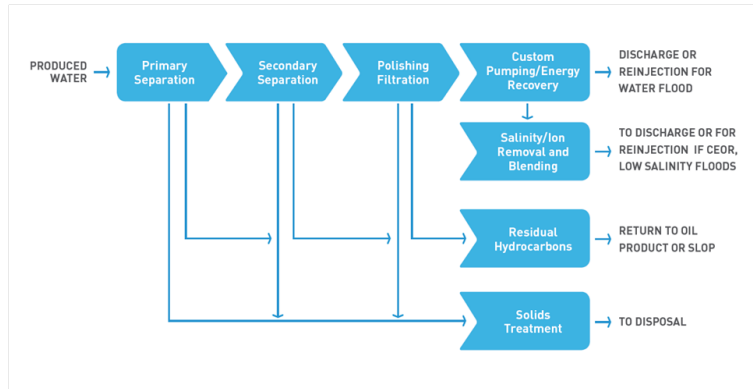


Figure 1.1: Offshore produced water treatment

a well defined mathematical model[7].

Currently there are three types of models to explain the mechanism of colloid transport in porous medium: the delayed drops models[8][9], the bulk viscosity model by Alvarado and Marsden [10], and the filtration model[11]. Among the three, filtration model is the most accurate and accepted. In this model the emulsion transport mechanism was compared to that of a deep bed filtration. These mechanisms are discussed in detail in the theory chapter. Several experimental studies have been done which support the validity of the filtration model. A packed column experiment was employed in most of these studies to understand the flow mechanism and the parameters affecting the transport. Having said that little effort was taken to actually visualize what is happening in the porous medium. The idea of a custom built cell to visualize the capture the droplet evolution in the porous media with the help of a microscope is what makes this project different and relevant. In this project, the porous medium was observed through the transparent glass window throughout the course of the experiments. A real time image of the cell along with the analysis of the outlet droplet distributions can give a much better understanding about the mechanism.

Background Information

The term produced water includes both formation water and the water injected containing production chemicals. Formation water means the water which has been trapped in the earth core along with the oil and gas for millions of years. During the drilling process this water comes to the surface along with the hydrocarbons. In addition to this, sea water or fresh water is injected to the reservoir to increase the well pressure causing an improved oil recovery. This water will also penetrate to the production zone and comes out with the hydrocarbons[12]. PW represents the largest volume by-product and in 2003 an estimated 667 million metric tons of produced water were discharged into the ocean from all around the globe[4]. The amount of water produced depends mainly on the age and location of the well. The ratio of water to oil (WOR) or water to gas ratio (WGR) varies from 0 to up to 50 based on the age and location. The amount of water produced increases as the well ages[13]. The production composition will be 98% PW and 2% fossil fuel for nearly depleted wells[14]. There is a considerable concern about the discharge of PW into the ocean since discharge is a continuous process and the volume of PW increase over time which cause the treatment methods less efficient causing a discharge of toxic chemicals into the ocean[4].

2.1 Chemical composition of produced water

Produced water is a complex mixture of dissolved and particulate organic and inorganic chemicals. The nature and the chemical composition of the PW depends on the location of the well, age, depth, and the geochemistry of the well. It also depends on the production techniques employed and the production chemicals used. As mentioned already, no two wells will have the same composition of PW. A general composition of PW is discussed in this section.

2.1.1 Organic chemicals

The concentration of total organic carbon (TOC) ranges from less than 0,1 to more than 11,000 mg/L[4]. The organic part of PW consists of organic acids and petroleum hydrocarbons such as BTEX and benzenes. The organic acids represent the major part of the organic components in PW and are usually mono- and di- carboxylic acids (-COOH) of saturated and aromatic hydrocarbons[4].

Formic acid is the most abundant among the acids and the abundance decreases as the molecular weight increases[15]. The low molecular weight organic acids are biodegradable by organisms such as bacteria and fungi and hence become nutrient for plankton growth[16]. Naphthenic acids can also be found in the PW especially when the hydrocarbons undergo bio-degradation in the formation. Naphthenic acids are slightly water soluble and will be present in the PW if the oil has a high content of it[17]. Naphthenic acids include series like alkylated benzoic acid, salicylic acid, and varieties of naphthoic acids[4]. Naphthenic acid in produced water causes corrosion in pipelines due to acidity and also contribute to the toxicity of the produced water[18]. It is also a surface active agent which stabilizes the oil in water emulsion causing it difficult to remove the oil from water[19].

Other organic components in PW are the hydrocarbons which cause a great environmental concern. Hydrocarbons present in PW as both dissolved and dispersed. Saturated and aromatic hydrocarbons can be found in PW and aromatics are more soluble than the saturated hydrocarbons in water. The molecular weight is also a factor which controls the solubility. Solubility decreases as the molecular weight increases[20]. Polar components are the cause of solubility of oil in water while temperature and pH play a role too[21]. Dispersed oil droplets usually form a oil in water emulsion, which is stabilized by the surface active chemicals present in crude oil and the production chemicals. Treatment methods such as hydro cyclones or gravity separator are used to remove this oil from water. A 100% removal of dispersed oil is not possible, even though near to 100% can be achieved using tertiary cleaning methods like media filtration. The factors affecting the concentration of the oil in PW are interfacial tension between oil and water, oil density, and the type and efficiency of the chemicals used and that of the separation equipment[22]. Discharge of oil into ocean causes the contamination of ocean sediments at the floor and also can rise to the surface causing sheening and increased biological oxygen demand[14].

2.1.2 Inorganic components

The major inorganic components present in PW include salt, treatment chemicals, produced solids, scales, metals, and radioactive elements. The PW contains similar salts as sea water with Na^+ and Cl^- being the major ions, but the concentration is higher than that in sea water giving rise to a higher density for PW compared to sea water[23]. The salinity varies from a few parts per thousand to that of concentrated brine[4]. Treatment chemicals used during drilling process and downstream operations can find its way into the PW which cause environmental impacts. Another major component is metals. The presence and concentration of metals in PW depends largely on the geography and age of the well, even though a direct relationship between the concentration of metals in oil and that in PW is not visible[24]. The typical metals found in PW are manganese, zinc, iron, lead, and barium. Even though the metal concentrations are higher in PW compared to sea water, the potential impact on the marine environment upon discharge to the ocean is low due to dilution. Furthermore these metals get adsorbed to the sediments causing it less bio-available to the marine animals[14]. Naturally occurring radio active materials are also present in produced water such as radium-226, and radium-228[25]. Chemical composition of produced water from Norwegian north sea platforms is given in the table 2.1*

*Table is taken from Produced water 2 edited by Mark Reed and Stle Johnsen and written by James P Ray

2.1 Chemical composition of produced water

Table 2.1: Chemical composition of produced water from Norwegian north sea platforms

Fields	unit	Statfjord	Gullfaks	Ekofisk 2/4B-K	Ekofisk 2/4T	Tor	Ula
Compounds							
TOC	mg/L	850	61	180		85,5	71
THC	mg/L	15	35				50
Sum aromatics	mg/L	6,00	9,56	5,67	66,95		15
BTX	mg/L	4	5	5,41	66,90	1,1	12
Naphthalenes	mg/L	0,942	2,16	0,247	0,052	0,597	
Phenanthrenes	μg/L	45	90	6,26	0,28	135	
Dibenzothiophenes	μg/L	8,6	22,7	1,39	0,15	10	
Sum NPD	mg/L	1,00	2,27	0,254	0,055	0,74	
acenaphthylene	μg/L			0,89	0,02		
Acenaphthene	μg/L	0,001	0,001	n.d	0,04	0	
Fluorene	μg/L	12	11,3	n.d	0,33	8,1	
Fluoranthene	μg/L	0,0854	0,195	n.d	n.d	0,24	
Pyrene	μg/L	0,0897	0,194	n.d	0,08	0,42	
Chrysene	μg/L	0,226	0,398			0	
Benz(a)anthracene	μG/L	0,0193	0,311	n.d	n.d	0,23	
Benzo(a)pyrene	μg/L	0,001	0,001	n.d	n.d	0	
Benzo(ghi)perylene	μg/L	0,001	0,001	n.d	n.d	1,35	
Benzo(k)fluoranthene	μg/L	0,0197	0,0528	n.d	n.d	0,016	
Sum PAH 3-6 ring	μg/L	66,04	125,15	0,89	0,47	155,36	
Sum phenol	mg/L	8,3	2,7	1,03	2,65	3,62	0,09
Phenol	mg/L	5,1	0,8	0,61	0,97	2,19	0,033
Sum organic acids	mg/L	895	55	323	577	234	
Methanol	mg/L			6,3	33,9		
Salinity Cl-	mg/L			30400		90500	40440
Amonium	mg/L	25,4	26,9				0,1
Lead	μg/L	50	50	n.d		806270	
Copper	μg/L	2	2	20		600	20
Iron	mg/L			4		8,9	23
Barium	mg/l			28,2	642,1	12	
Cr-VI	μg/L	10	10	6		0,08	40
Mercury	μg/L	1,9	1,9	n.d			9
Zinc	μg/L	6,8	13	13		200	0,26
Cadmium	mg/L	10	10	n.d			0,02
H ₂ S	mg/L	0,12	0,17				

2.2 Produced water Management

The amount of water produced increases as the well ages and hence the handling of this water is a major concern. The method adapted to handle the water depends on the location of the production site, cost, environmental regulations, technical feasibility, and the availability of equipment. The main available methods at disposal for handling PW are discharge, beneficial reuse, and re-injection. Discharge used to be the primary method. As the regulatory requirements became stringent leading to a more expensive treatment method, companies started to look into alternative options. The companies started to recognize water as a value to the operation rather than a waste stream. For example Shell introduced the program called water to value which focus on reducing the production of water and also to treat more water at the existing facilities[26]. Companies are more focused on reducing the water production nowadays. Some of the methods used to reduce water production are discussed below.

2.2.1 Blocking Water

Preventing the water from entering the production stream is one of the method to reduce the water production. The methods in use nowadays are chemical shut-off and mechanical blocking. In chemical shut-off the idea is to shut-off water while maintaining a continuous production of oil by the help of chemicals. The shut-off chemicals are injected into the formation where it selectively block the water pathways causing a reduction in water production. Most of the chemicals used are polymer gels or pre-gel forms[4]. Since the chemicals are being injected deep into the earth, it will not affect the biosphere. Another way of blocking the water from entering the production stream is to mechanically block the water. Mechanical blocking devises include straddle packers, bridge plugs, tubing patches, cement, and well bore sand plugs[27].

Once the water is produced, the next step is to dispose it. The common methods of disposing the PW are discharge into ocean, reuse for beneficial purposes, and re-injection into the formation to increase the pressure and enhance the oil recovery.

2.2.2 Discharge into Ocean

Discharge into ocean was the most common method of PW disposal. Since the PW contains a lot of toxic chemicals, it pollutes the ocean environment. As the concern about environment increased, regulatory bodies are formed all around the globe which set the limit for different components in the PW. So it is required to treat the water prior to discharge. a typical treatment diagram is shown in the Figure2.1[28].

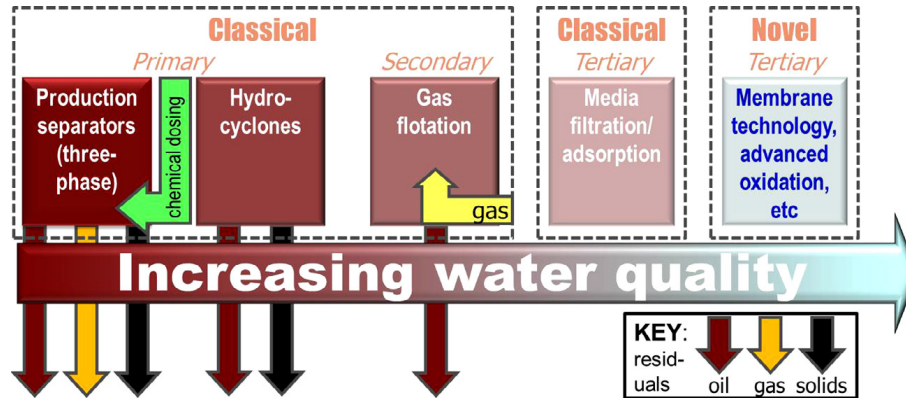


Figure 2.1: Offshore produced water treatment

The treatment operation includes three sections, first the primary treatment followed by secondary and tertiary treatment. The primary treatment includes the gravity separation and hydro-cyclone which is mainly focused on removing the dispersed oil content from PW. The gravitational and centrifugal forces are used to separate the oil from water. These treatments are not highly efficient and a complete removal of oil is not possible. Further removal of oil is done in secondary treatment section where gas flotation is used to remove oil. A oil removal up to 70% is possible using this method. A near to 100% oil removal and other chemicals removal can be achieved by tertiary treatment methods like media filtration. These treatments are effective in removing dispersed oil and other components but the dissolved oil will still be present in the PW which is discharged to the ocean[18]. But experience from off-shore shows that if the dispersed oil is removed the dissolved and volatile oil concentration are reduced to acceptable level[29].

2.2.3 Beneficial reuse

Beneficial reuse of PW includes use by animals, irrigation, and industrial use. Some produced water is clean enough, after some degree of treatment and sometimes without any treatment, to be used by animals. The livestock have a higher tolerance to the contaminants in the drinking water. Water with total dissolved solids(TDS) lower than 1000 ppm is considered to be fit for drinking, while cattle can tolerate up to 7000 ppm with a slight possibility for diarrhea[30].

Irrigation is the single largest consumer of fresh water in USA and other parts of the world[26]. The PW water can be used for this purpose if it can meet the requirements for irrigation water. The main parameters to be considered here are salinity and the toxicity of the PW. The PW needs to be treated to bring down the salinity and other components to the desired level. PW is already being used for irrigation in some places such as Wyoming[30] and California[31]. Produced water can be used in industries also for purposes such as vehicle and equipment washing and dust control.

2.2.4 Re-injection

Sea water has been the fluid used to maintain the reservoir pressure until recent years. But the trend has taken a turn towards PW being used for this purpose instead of being dumped into the ocean in the recent years. This happened due to the benefits of using PW such as less pollution, less scaling

problems due to sea water in the pipe lines, and less risk of H₂S formation in the reservoir[32]. In addition the reduced cost of treating the water encouraged companies to inject more PW back to the reservoir. Further improvements have been done to reduce the operation cost such as separation and re-injection of water at subsea level to avoid the transportation cost to and from the platform[33].

2.2.5 Challenges in re-injecting the water

Even though the re-injection has the benefits like reduced pollution and reduced operating cost, it faces some challenges too. Water incompatibility is a big issue when it comes to injecting PW. The water produced from one well is not enough to provide sufficient pressure. So PW from several wells need to be mixed. These water will have different temperature, pressure, pH and chemical compositions[34]. This difference cause the treatment difficult and also make the water incompatible. The main challenges are injectivity decline and formation damage[35]. Field studies showed that a 20 to 40% reduction in injectivity occur when PW is used for reinjection compared to sea water[36] Formation damage can occur due to several factors such as pressure, temperature, and solid present in the PW. Fractures occur when the injection pressure at the bottom hole is higher than the reservoir compressive stress[36]. SO the operation needs to be carried out below that pressure to keep the integrity of the well. Even when the operating pressure is lower, some times the injected water have a temperature colder than the well causing a contraction of the well. This contraction cause a reduction in stress and the operating pressure becomes sufficient to cause formation damage[36]. The solids present in the PW will also cause damage to the well, affecting the porosity of the well. The formation of external cakes which act as a filter and retention of oil droplets inside the formation causing a blockage of the path are the reasons for this. Further more a well defined model for emulsion transport is not available and the quality requirement for PW varies from location to location and also from well to well. So selection of treatment methods are not easy and have to depend solely on the experience and the practical knowledge about the well.

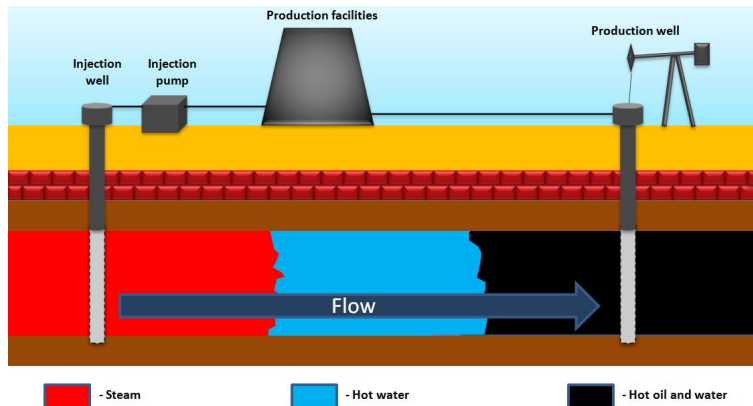


Figure 2.2: A reservoir with injection and production wells*

*Picture taken from the article: Acrylamide in Environmental Water: A Review on Sources, Exposure, and Public Health Risks

Theory

3.1 Colloidal system

The term colloid (from the Greek word colla, meaning glue) was first introduced by the Scottish chemist Thomas Graham in 1861. He was measuring the diffusion rate of different chemical compounds in water and found out that some polymeric compounds diffuse slower than the inorganic salts. He named this group as colloids as the polymeric compounds were viscous and glue like. A colloid system is a homogeneous system formed by two immiscible components. A colloidal system consists of a dispersed phase and a dispersion medium. The dispersed phase consists of droplets of size ranging from 1 nm to 1 μm dispersed in a continuous phase called dispersion medium[37]. An important property of the colloidal system is the high surface to volume ratio. This high surface to volume ratio arises due to the reason that the compound is dispersed as micron size range droplets. Hence the surface properties are important in case of colloidal solutions.

Colloidal systems can be classified in numerous ways based on its chemical and physical properties. It can be classified into lyophilic and lyophobic based on its affinity towards liquid(hydrophilic and hydrophobic if the liquid is water). Inorganic and organic classification based on the chemical composition.

Based on the state of the continuous and dispersed phases, colloids have different names. One of the important group of colloids in this category is emulsion. Emulsions are colloids which have both dispersed and continuous phases in liquid state. Emulsions have a very important role in our daily life. From the milk we drink to the paint we use on the wall are all emulsions. Most of the emulsions occur as poly dispersed with wide spread of droplet sizes. The emulsions are classified into normal emulsions and micro emulsions. The key factor which distinguishes micro emulsion from normal is the stability, which is discussed in detail in the next section.

3.2 Colloidal stability

The concept of stability of a colloidal system means the ability of the dispersed phase to stay dispersed and not to be separated into a distinct layer. In other words the ability of the dispersed droplets to resist coalescence. The lyophilic colloids form true solution instantaneously and hence

are stable infinitely, unless some kind of disturbances are introduced such as change in pressure or temperature. In case of lyophobic colloids, a spontaneous formation of true solution is impossible. For systems like water and oil an external energy is required to form the colloidal solution but upon standing phase separation will occur. The cause of separation is gravity. Upon standing the gravity will act on the dispersed phase causing it to sink to the bottom or rise to the top based on the density. For the gravitation force to have some effect on the dispersed phase, the droplets should have a certain size. At sub micron ranges the droplets are not affected and stay in the solution. But as the time laps, droplets come closer and attach to each other and grow bigger. There are several reasons why this fusion of droplets happen. One such reason is flocculation. The droplets come closer and get attached to each other. Main reason for this attraction is the ever existing van der Waals force. The van der Waals force keep the droplets together causing the gravity to act and based on the density of the phase compared to continuous phase, the droplet either rise to the top or sink to the bottom. Sometimes these attached droplets can fuse together and form a single bigger droplet, which is also influenced by the gravitational force. This phenomena is called coalescence. Another plausibility for the droplet to grow bigger is by Ostwald ripening. This is a phenomena where bigger droplets grow further at the expenses of the smaller droplets. This is governed by the pressure inside the droplets or the pressure acting on it. All these effects tend to make the dispersed droplets to come together and get separated under the gravitational force. Based on this tendency of dispersed phase, the colloidal system posses two types of stability which are kinetic stability and thermodynamic stability.

3.2.1 Thermodynamic stability

A colloidal system is thermodynamically stable means the formation of a solution is favoured by thermodynamic than staying as two separate layers. This means that the Gibbs free energy of the total system will be lower when it is in colloidal state compared to two separate layers. All the lyophilic systems are thermodynamically stable. Other examples of thermodynamically stable systems are micro emulsions and micelles. The micro emulsions are thermodynamically favoured where as the normal emulsions are kinetically stabilized.

3.2.2 Kinetic stability

As we discussed emulsions are thermodynamically unstable. This means the system tend to separate into two phases. The rate of separation is not constant. Some systems will separate immediately once it is allowed to stand whereas some systems take days, months and even years to separate. Such systems, where the rate of separation is very low, look stable in the given time frame. These colloids can be said kinetically stable even though the thermodynamics does not favour the colloidal state. The particles in the dispersed phase are always under movement due to Brownian motion. These motions can cause the particles to come close and if the particles are close enough for the van der Waals force to act, the particles will form a flock of droplets like a bunch of grapes which eventually coalesce and be separated into another layer. The phase separation can be prevented if the contact between particles are prevented. Any situation or parameter which can prevent the particle contact will give rise to stability of the system and hence the system can be

called kinetically stable. In simple words the ability of the system to prevent particle contact is the one giving kinetic stability to the system. There is an energy barrier to overcome in order for the droplets to come in contact and if the thermal energy of the system is lower than this required energy, the system will stay stable. A representation of this energy barrier is given in the Figure 3.1*. Kinetic stability of a colloidal system can be achieved in several ways and they are classified

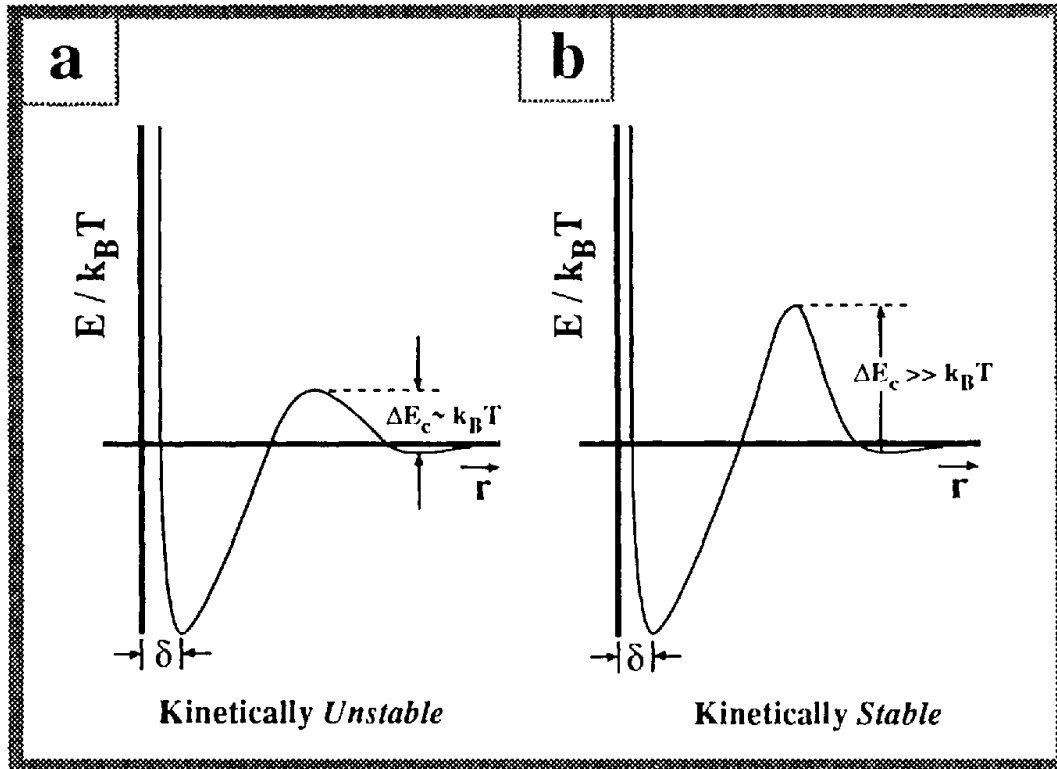


Figure 3.1: Kinetic stability of a colloidal system

into

1. Electrostatic stability
2. Steric stability
3. Electro-steric stability

When the aggregation of two droplets is prevented by the same charge present on the surface of the droplets, the system is said to be electrostatically stabilized. The electrostatic repulsion between the two charged droplets is the reason for the stability of the colloid. Surface active ionic chemicals can be used to impart electrostatic stability to a system.

A system is called steric stabilized if the bulky molecules on the surface of the droplets prevent the droplets from coming into contact and coalesce. Here the repulsion is not because of the charge on the surface but due to bulky molecules which provide a steric hindrance. Surface active non-ionic polymers impart steric stability.

*Figure taken from the book Principles of colloid and surface chemistry, third edition by Paul C. Heimenz and Raj Rajagopalan

When the aggregation of droplets are prevented by both electrostatic repulsion and the steric hindrance, then the system is electrosterically stabilized.

3.3 DLVO theory

The surface potential of the dispersed particles is an important parameter in calculating the kinetic stability of the colloidal system. The particles experience both attractive and repulsive forces based on the surface charges and distance between the particles. An interaction energy curve with distance between two particles as horizontal axis and interaction potential as vertical axis can be used to quantify the kinetic stability of a colloidal system. Such a study of the kinetic stability is called Derjaguin-Landau- Verwey-Overbeek (DLVO) theory, derived simultaneously by Russian physicists B. Derjaguin and L. Landau and the Dutch pioneers in colloid chemistry, E. Verwey and J. Th. G. Overbeek. The particles experience an attractive force between each other due to the always present van der Waals attraction, which can be calculated using the equation 3.1.

$$V_A = -(Ad/24l) \quad (3.1)$$

van der Waals force is by convention negative and increases as the distance between the two particles decreases. Particles will also experience a repulsive force due to the surface charges, which can be calculated using the equation 3.2.

$$V_R = (1/4)\epsilon d\zeta^2 \exp(-\kappa l) \quad (3.2)$$

where d is the diameter of colloidal spheres, l is the inter particle distance, A is the Hamaker constant, ϵ is the dielectric constant of the solvent, ζ is the zeta-potential, and κ is the reciprocal ionic concentration.

The net force V_T is then given by the equation 3.3.

$$V_T = V_A + V_R \quad (3.3)$$

If V_T is negative, attractive force dominates and the particles will coalesce leading to instability of the colloid and if it is positive the colloidal system will be kinetically stable. An example of the inter-particle interaction energy curve is given in Figure 3.2[38]. The red line shows the repulsive force and blue line represents the attractive force. Black line shows the total interaction potential and the shown energy barrier needs to be overcome in order for the droplets to coagulate and if the system does not have required energy to overcome this barrier then the colloidal system will be stable.

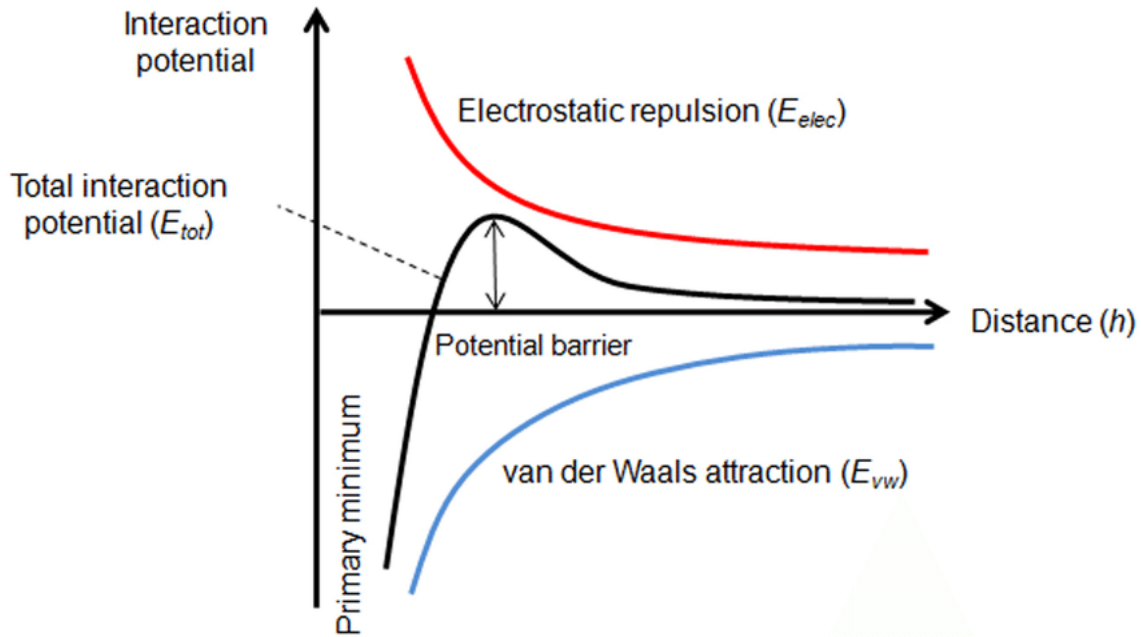


Figure 3.2: Inter-particle potential energy curve

3.4 Transportation models for emulsion flow in porous media

There are currently three models to explain the mechanism of emulsion transport through porous media, which are: the delayed drops models[8][9], the bulk viscosity model by Alvarado and Marsden[10], and the filtration model[11]. The bulk viscosity model assumes emulsion as a continuum single phase. It also assumes no interaction between the droplets and the porous wall, even when the size of the droplets and the porous opening are comparable. The porous medium scaling law is employed in explaining the model mathematically[39]. The drawbacks of this model are no permeability reduction is predicted and the droplet breakthrough is expected in one pore volume. The experimental researches disprove these assumptions except in the case of emulsions with very high concentration[40]. The permeability reduction is considered in the delayed droplet model but it also failed to explain an irreversible reduction in permeability[7]. This model suggests that when a droplet having a diameter larger than the pore opening, it is squeezed in by deformation and as a result experiences a capillary resistance force. This resistance cause a reduction in the transient permeability[9]. The filtration model is considered as the most accurate in explaining the mechanism of colloidal transport through porous media among the three models. This model is discussed in detail in the next section.

3.4.1 Deep bed filtration model

The filtration models compares the emulsion transport through porous media to deep bed filtration. Two types of droplet capturing mechanisms are considered in this model, which are

1. Interception

2. Straining

The droplets which are bigger than the porous opening cannot enter the pore channels. These droplets form a layer on the surface of the porous media similar to a filter cake[41]. Some of the droplets smaller than the porous opening will also be trapped inside the channels by mechanical capturing in the narrow regions inside the channels. This capturing of droplets by mechanical entrapment is called straining. The reason for straining is simply the geometry of the droplets and the porous medium. It occurs mostly at the surface and also inside the channels where there are congestion. The droplets which are small enough to avoid the straining can be captured by the mechanism called interception. Here the capturing mechanism is governed by the physical and chemical interactions between the droplets and the wall. The common interactions include van der Waals attraction and electrostatic attraction due to the opposite charges on the surface of the droplets and the wall. This type of capturing mechanism is called interception[11]. A graphical representation of the deep bed filtration model is given in Figure 3.3*.

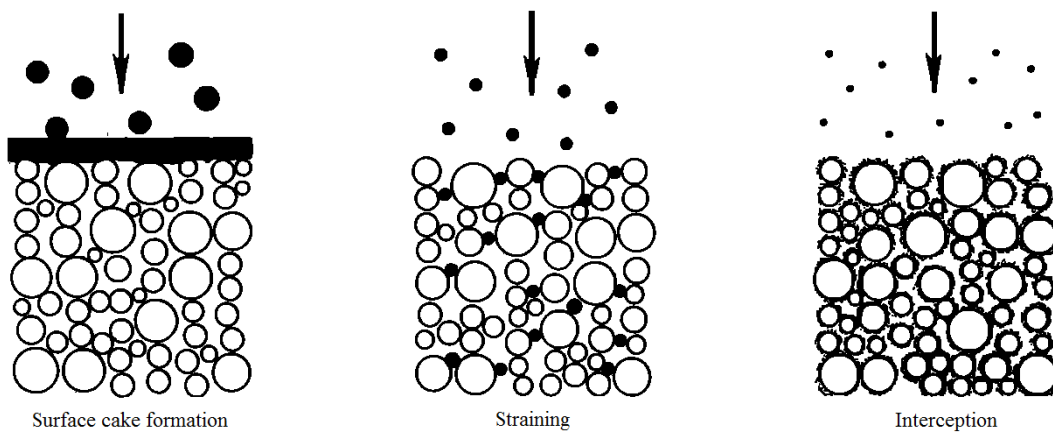


Figure 3.3: General filtration mechanisms

3.4.2 Travelling globule mechanism

It is an alternate transport mechanism coined by Spielman and Goren. As per this mechanism, suspended droplets grow on the fibres by further capture and coalescence until they eventually grow so large that the hydrodynamic force cause them to break away from the surface. Lloyd A. Spielman and Yeang-Po Su proposed the existence of three distinguishable regimes of the coalescing phase in the porous medium[42] which are

1. Oil droplets suspended in the aqueous phase
2. Coalesced oil forming a continuous phase and flowing in well connected channels
3. Held-up oil as discrete coalescing globules that act as an intermediate between the dispersed oil droplets and the continuous oil phase.

*Figure taken from the literature particle transport through porous media by Laura M. McDowell-Boyer, James R. Hunt, and Nicholas Sitar, vol.22

3.5 Transport of stable and unstable colloids

The permeability reduction is obvious in case of transport of unstable colloids through porous media due to the fact that the droplets coalesce and form bigger droplets. J.A.M.H. Hofman and H.N. Stein from Eindhoven university of technology have conducted experiments with unstable colloids and the results agreed to the permeability reduction[43]. A matched density emulsion was used in their experiments to avoid the segregation effects due to density difference. A mixture of n-decane and tetrachloromethane has been selected as the dispersed phase. The composition of the dispersed phase was chosen such a way that the mixture density matches with that of the aqueous solution which was used as the continuous phase. A glass column packed with glass beads was used for the experiment. Permeability reduction was observed after passing the emulsion through the packed column. In addition, a considerable lowering of permeability reduction was observed when the colloid was stabilized with sodium oleate.

Given said that the permeability reduction is quite low for stable colloids, the reason for droplet entrapment for colloids having droplet sizes smaller than the pore opening needed to be investigated. One of the important studies about transport of stable colloids was done by McAuliffe in 1973[9]. In this study an oil in water emulsion of crude oil and water was passed through a packed column. The packing material used was Boire, Alhamba, and Berea outcrop sandstone cores fired at 400°C. The findings from this study were that the permeability reduction occurs in case of stable colloids also and the permeability reduction is higher for larger droplets. Furthermore, it was observed that the permeability reduction is irreversible. The flushing of the core with distilled water for almost 15 pore volume resulted in only a slight increase in the permeability.

One of the pioneer study about flow mechanism of dilute stable emulsion in porous media is done by Hwalll Soo and Clayton J. Radke[44]. Refined mineral oil stabilized with sodium oleate and oleic acid is used as a dispersed phase and distilled water-sodium hydroxide solution as continuous phase in these studies. The porous media was a stainless steel cylinder filled with sand. The pressure drop across the column and the outlet concentration and particle size distributions were monitored to understand the transport mechanism. A plot of permeability reduction against the pore volume injected showed a good agreement with the flow theory[11]. One important finding from these experiments was the permeability of the porous medium reduces as the emulsion passes through it and eventually reaches a steady state. Once the steady state is reached, then the outlet will have the same concentration as the inlet. This finding discredited the bulk viscosity model [10]. After the emulsion transport, the packed column was flushed with distilled water to check the reversibility of the permeability. A significant increase in the permeability was not observed. It was in disagreement with the droplet retardation model, as per which the permeability is reversible. This experiment showed that the droplet retardation is not the primary mode of droplet capturing. To further understand the physical mechanism of colloid transport in porous media, a micro model was built where Soo and Radke observed the flow behaviour under a microscope. This visual observation also agreed with the deep bed filtration theory where the main mechanisms of droplet retention are straining and interception. Secondary attachment of droplets by the already attached droplets was not observed in this experiment.

3.5.1 Parameters affecting the transport and effects

The main factors affecting the transport of emulsion through porous media are

1. Drop size to pore size ratio
2. Stability
3. Wettability
4. Velocity
5. Surface chemistry of the emulsion and the porous media such as the pH and ionic strength of the emulsion.

We have already discussed the effect of droplet size and the stability of the colloid on the transport through porous medium. Several studies have been done to understand the effect of different parameters on the emulsion transport and some of the important studies are discussed here.

The effect of pH and ionic strength was studied by Jayaprakash Soma and Kyriakos D. Papadopoulos[45]. An emulsion of n-hexadecane in deionized water was used, which was passed through a porous medium of white quartz sand. Inlet and outlet concentration and droplet size distributions were monitored. An increase in permeability reduction was observed as the pH decreased. The droplets were negatively charged and were hence electrostatically stabilized. As the pH decreased, the concentration of H^+ ions increased which neutralized the surface charge. This resulted in stability loss and coalescence lead to higher permeability reduction. Similar effect was observed in case of change in ionic strength. As the ionic strength increased, stability reduced and permeability reduction increased.

An interesting effect of interfacial energy was observed in experiments conducted by J.A.M.H Hofman and H.N Stein[43]. Two different stabilizing agents were used in this experiment, which were sodium oleate and Aerosol OT(sodium dioctyl sulphosuccinate). Emulsion formed using AOT has a lower interfacial tension compared to the one with sodium oleate. It has been found out that the emulsion with AOT caused a higher permeability reduction. This can be understood from the relationship between interfacial tension and the stability of the colloid. When the droplet having a lower interfacial tension approaches a pore constriction, the droplet deforms and adapt the shape of the wall easily. This happens because the droplet needs a small amount of energy to deform. Once a flat contact area is formed between the droplet and the wall, coalescence is possible because the low interfacial tension leads to only a slight additional surface energy for the squeezing mode of interface disturbances which initiates fracture of a thin liquid film[46].

Wettability of the porous medium is an important parameter in understanding the emulsion transport mechanism. Most of the early studies were modelled based on the assumption that the oil rocks are water wetting[47], oil wet or intermediate wet[48]. But later researches showed that most of the oil rocks have heterogeneous wettability[49]. From studies it has been found out that water wetting surfaces have lower permeability reduction when the emulsion is being passed through it[50]. The interception is more plausible when the surface is oil wetting. Another study done by C. Shin and G.G. Chase[51] with water in oil emulsion also suggests that in order for the dispersed phase to get attached the surface, the dispersed phase need to be preferentially wetting then the continuous phase. There are several ways to alter the wettability. One of the methods is salinity. The brine solution will alter the affinity of oil towards the porous medium. the effect is different for different oil samples. The effect of salinity is not just the change in wettability. It

also alter the droplet distribution[52] and interfacial elasticity[53]. The overall effect of salinity on emulsion transport will be based on which among the above stated parameter is affected the most by salinity change. The effect of fluid velocity on emulsion transport was studied by Soo and Radke[54]. Their studies showed that at high injection velocities, the droplets captured by straining can squeeze through the porous medium if the local pressure gradient overcomes the capillary force.

Materials and Methods

4.1 Materials

Hexadecane is obtained from SigmaAldrich(laboratory grade, purity 99%) and used as received. Cetyl trimethyl ammonium bromide (CTAB) was purchased from SigmaAldrich, Glass beads acid washed from Sigma Aldrich(150-212 μm , 425-600 μm , 710-1180 μm). Sudan IV dye(dye content 80 %) from SigmaAldrich. The two crude oil distillate cuts were obtained from a Ph.D. candidate at the Ugelstad lab, Jost Ruwoldt. The crude oil cut were labelled as light cut and heavy cut based on the density of the distillate cuts, Crude oil(Beta)[55], MQ water, NaCl purchased from Sigma Aldrich.

4.2 Injection cell

This is a continuation of the specialization project done in fall 2017 as a part of the curriculum. The specialization project was mainly focused on the modification of the basic cell design adopted from the work of Anders Andersen, a master student in the department of chemical engineering at NTNU. The cell consists of three main parts. A bottom base, a middle section, and a top part. All these parts are made of stainless steel, which are shown in the Figure 4.1. The inlet and outlet are connected on the bottom plate. The bottom plate and middle plate are connected together with screws. A glass plate is glued to the surface of the middle plate which acts as the visualization window. Top part is to support the glass plate. A detailed description of the cell can be found in the specialization project written by Prajin Joseph[1]. An improvement to the existing design has been done to ease the glass beads loading procedure and also to achieve a tight packing. A hole had been drilled on one side of the middle plate, which opens to the packing space. This hole can be closed with the help of a screw coated with Teflon tape.

A funnel which can be inserted into the loading hole is used to load the glass beads through the hole. Care has been taken to make sure that the glass beads are tightly packed but would not break the glass window upon closing the opening. After the glass beads have been loaded, a screw wrapped with Teflon tape was used to close the loading hole. The weight of the cell was noted before and after which was used to calculate the porosity of the cell by weight method. After the

experiments, the glass beads were taken out through the same hole to clean and dry in the oven. The cell was flushed with acetone to take out all the beads and the beads were washed and dried in the oven at 55°C overnight.

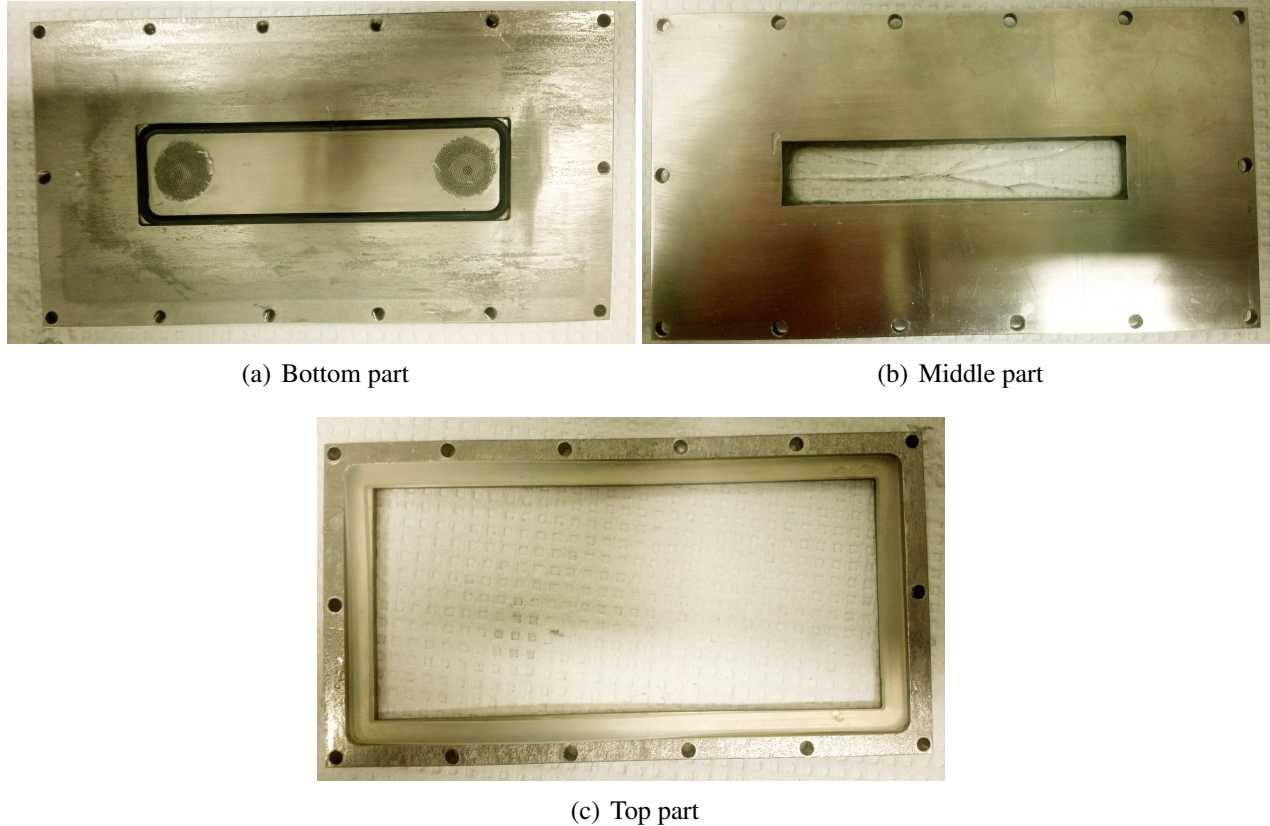


Figure 4.1: Parts of the cell

4.3 Colloid preparation

A stable colloidal solution was used throughout the project. Cetyl trimethyl ammonium bromide (CTAB) was used as the surface active agent. An Ultraturax mixer was used to prepare the emulsions. Four different dispersed mediums were used in this project, which are hexadecane, crude oil light cut, crude oil heavy cut, and crude oil(beta). Emulsions were prepared at a concentration of 0,1 v/v %. The CTAB was first dissolved in the continuous phase, which was MQ water. The amount of CTAB was chosen such that the concentration of CTAB will not exceed the critical micelli concentration (1,0 mM). The dispersed phase was added to the CTAB solution and emulsion was prepared using Ultraturax. Sudan IV dye was used to aid the visualization of the oil droplets. Sudan IV was dissolved in the oil before it was mixed with the continuous phase. The speed was adjusted according to the droplet size requirement. In this project, 4500, 7500, and 15000 rpm were used. The colloid was mixed for 2 minutes and later analyzed under microscope to calculate the initial droplet size distribution.

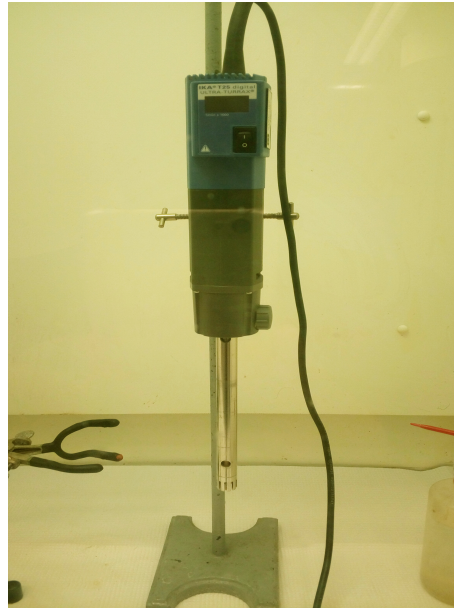


Figure 4.2: Ultraturax

4.4 Characterization techniques

Image analysis was used to calculate the droplet size distribution at the inlet as well as the outlets. The sample was collected in a glass cuvette similar to the one shown in the Figure 4.3. The cuvette was observed under a Nikon Eclipse LV100 microscope and the pictures were taken using the camera.



Figure 4.3: Cuvette for measuring the drop size distribution



Figure 4.4: Bright field microscope

In order to normalize the pictures, the cuvette was allowed to stand for one minute before the pictures were taken. A total of 10 pictures were taken for every sample from different parts of the cuvette in order to get an average distribution. A 20X magnification lens is used for all the measurements. After the picture were taken, ImageJ software was used to count the number of particles and also to calculate the average diameter.

The density of the oil cuts were measured by Anton Paar DMA 5000M- Density/concentration meter. The interfacial tension of different dispersed phases in different conditions were measured using the Data physics SVT20 Spinning drop tensiometer. The viscosity of the oil samples were calculated using Anton Paar MCR301 rheometer. The porosity of the injection cell was calculated using the weight method. The cell was weighed without the glass beads and then after filling the glass beads. The difference in weight was taken as the weight of the glass beads and is converted to volume using the density of the glass beads. The total volume of the empty space of the cell is calculated using the geometry of the cell and the difference between the cell volume and the glass bead volume was calculated as the void volume of the cell. A sample calculation of this method is given in *Appendix A.1*.

4.5 Injection experiments

Four sets of experiments were conducted as a part of this project. First the evolution of droplets over pore volume (PV) injection was studied. Then some of the parameters were changed such as the droplet size, bead size and the salinity of the continuous phase.

For all the injection experiments, a syringe pump was used to inject the emulsion. The syringe pump consists of a piston to move the syringe, two 5 ml syringes, and two pressure sensors to measure the inlet and outlet pressure. Q mix element software was used to control the flow and the continuous flow feature is selected in order to maintain a continuous flow. It used two 5 ml syringes which pumped the emulsion alternatively. While one was on injection mode, the other one was on refill mode.

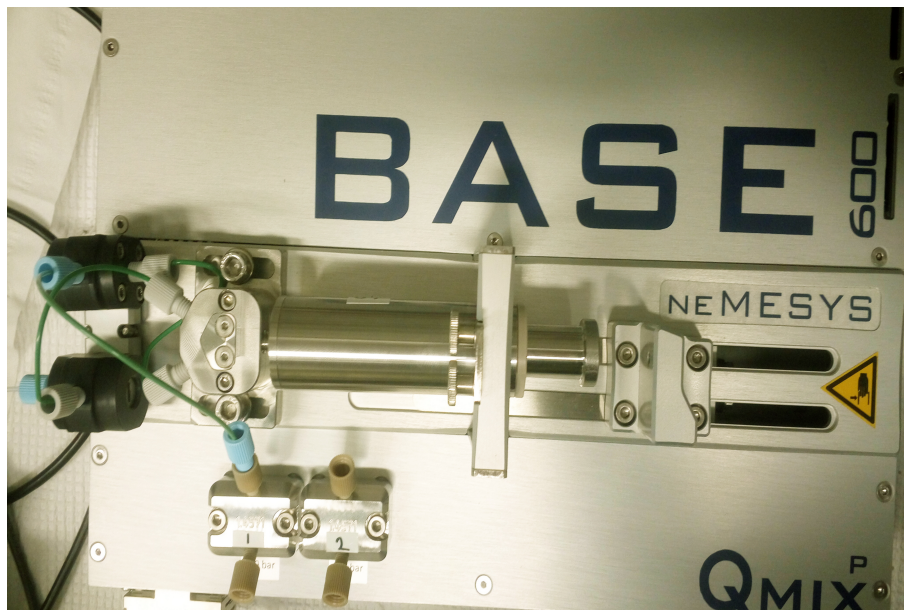


Figure 4.5: Syringe pump

The syringe fill the emulsion from the inlet reservoir, which then passes through an inlet pressure module(P1) to the injection cell. The outlet from the cell is passed trough another pressure module(P2) which measures the outlet pressure and to the outlet reservoir. Connectors of outer diameter 1/8 inch along with a ferrule of outer diameter 1/16 were used to connect the syringes to the injection cell. Teflon tubes of outer diameter 1/16 inch and inner diameter of 1/32 were used as the connecting tubes for all the parts. A flow diagram of the total flow setup is given in the Figure 4.6.

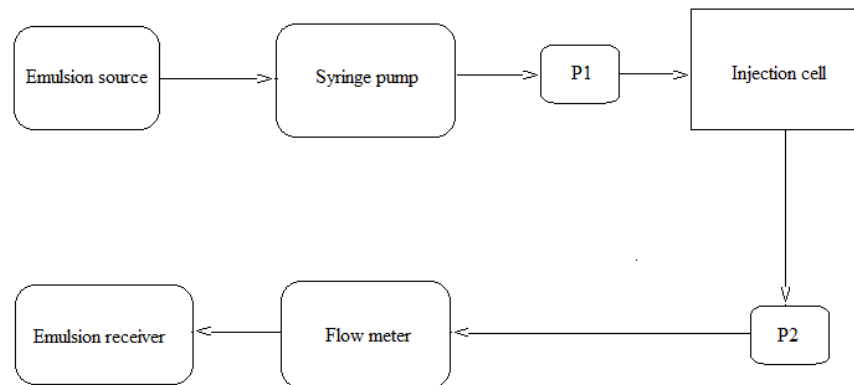


Figure 4.6: Flow diagram of the experimental set up

4.5.1 Pore volume evolution

In order to study the evolution of droplets over pore volume injection, a stable colloidal solution of hexadecane in water with CTAB as the stabilizer is prepared using Ultraturax at a mixing speed of 7500 rpm for 2 minutes. The Solution is then passed through the flow setup. The injection cell was saturated with distilled water prior to the start of the experiment. A flow rate of 1000 $\mu\text{l}/\text{min}$. was used in this experiment, which gives a superficial velocity of 0,022 cm/s. This flow rate was in accordance to the literature where a superficial velocity of 0,005 to 0,05 cm/s was used. Glass beads of diameter ranging from 150 to 212 μm were used in this experiments. In order to avoid the effect of creaming both the inlet and the outlet were kept under constant stirring using magnetic stirrer. The outlet was collected after passing 25 ml emulsion through the cell, which is equivalent to almost 16 pore volumes. The outlet is then sampled and droplet pictures were taken using the microscope. The experiment was continued and samples were taken after 50, 75, 125, 175, and 275 ml passing. The outlet was discarded after every sampling to avoid the mixing of two samples. This corresponded to pore volumes of 16, 32, 48, 80, 112, and 178. Two parallel experiments were conducted. The cell was cleaned and the glass beads were washed and dried in the oven before the second set of experiments to ensure the same initial conditions. In order to study the effect of different emulsions, the same experiments were repeated with two other model emulsions. The dispersed phase was replaced with two different oil distillate cuts instead of hexadecane. All other parameters were kept constant and only the dispersed phase was changed. All the pictures were taken and were analyzed using the ImageJ software. In addition the image of the cell was also taken to analyze the deposition of the oil droplets which was visible due to the Sudan dye in the oil droplets.

The same procedure was followed for the following sets of experiments, where the parameters were changes according to the experiments.

4.5.2 Effect of Flow rate

In this experiments all the parameters except the flow rate were kept constant. First set of experiments were conducted at a flow rate of 1000 $\mu\text{l}/\text{min}$. Then the flow rate was increased to 3000 $\mu\text{l}/\text{min}$ and the same experiments were repeated. Finally the flow rate was increased to 6000 $\mu\text{l}/\text{min}$ and the experiments were repeated. The glass beads were removed and washed, dried in the oven before the next set of experiments were started in order to ensure the same initial conditions and to make sure the observed effects were only due to change in flow rate.

4.5.3 Effect of bead size

In order to study the effect of bead size on the transport of emulsion through the porous medium, three different size ranges were used. The cell was first packed with the small beads having size range from 150 to 212 μm . The emulsion of same droplet distribution as the one used in the pore volume evolution analysis was used in this experiment also. All other parameters were kept the same such as flow rate. Then the same experiments were repeated with a packing material having a diameter ranging from 425 to 600 μm followed by glass beads having size range from 710 to 1180 μm . Similar to the previous experiments, the outlet was sampled after the 16, 32, 48, 80, 112, and 178 pore volume pass. The difference in the droplet distribution was analyzed to understand the effect of porosity on the transport of emulsion through porous media. In order to understand the response of different oils, the same experiments were repeated using the two oil distillate cuts. Two parallel runs were conducted for each experiments.

4.5.4 Effect of Droplet size

In order to study the effect of the droplet size on the transport of emulsions through porous media, Droplets having different diameter were passed through the porous media of same porosity. The glass bed of diameter ranging from 150 to 212 μm were used as the packing material and a flow rate of 1000 $\mu\text{l}/\text{min}$ was used. The different droplet distributions were achieved using different speed settings in the Ultraturax. First set of experiments were conducted using an emulsion of hexadecane in water, similar to the one used in other experiments, at a mixing speed of 7500 rpm. After the experiments were finished, a new emulsion was prepared using hexadecane and water with same surface active agent and the dye, but the droplet size was reduced by increasing the mixing speed to 15000 rpm. The same experiment was repeated with the new emulsion. Finally one more droplet size was tested which was prepared at a mixing speed of 4500 rpm. The outlet at the same pore volume passes of the three droplet distributions were compared to understand the effect of droplet size on the transport of emulsion. Further more the two oil distillate cuts were also used to conduct the same experiments and all the three mixing speeds were used also.

4.5.5 Effect of salinity

Three different aqueous solutions were used in this experiments which have different salinity. First set of experiments were conducted using MQ water as the continuous phase and the outlet was sampled after certain pore volume passing similar to the other experiments. For first set, hexadecane

was used as the dispersed phase with CTAB and Sudan IV. The effect of salinity was studied by varying the salinity of the continuous phase. A 20 mM sodium chloride solution and a 3,5 weight percentage sodium chloride solution were used. All other parameters were kept the same such as the emulsion mixing speed of 7500 rpm and the flow rate of 1000 $\mu\text{l}/\text{min}$. The results from the three different salinity tests were compared. The same experiments were repeated with light crude oil distillate cut and the results were compared. ‘

4.5.6 Test with Crude oil

To have a better understanding of the transport happening in the oil well during the injection of PW, a crude oil was used to make the emulsion. The crude oil-water emulsion was prepared in the similar manner as in other emulsions used in this project. CTAB was used as the surface active agent and ultra turax was used to form the emulsion. A higher mixing speed of 15000 rpm was used due to the stability issues of the crude oil. The pore volume evolution and the salinity tests were conducted using the crude oil. A flow rate of 1000 $\mu\text{l}/\text{min}$. is used in this experiments also and the small glass beads of size range 150 to 212 μm was used as the packing material. The droplet size test was not conducted due to the significant variation in the droplet size distribution and the stability issues. The same sample collection procedure was followed where the outlet was collected after certain pore volume passing. For the salinity test 3,5 wt% and 20 mM sodium chloride solutions were used as the continuous phase similar to the other experiments.

Results and Discussion

The properties of the four dispersed phases used in this project are given in the Table 5.1.

Table 5.1: Properties of the dispersed phases

Dispersed phase	Density(g/cm ³)	Viscosity(mPa.s)	Interfacial tension(mN/m)
Hexadecane	0,77	3,005	1,42
Crude oil cut- Light	0,8057	1,098	1,196
Crude oil cut- Heavy	0,8782	6,876	1,033
Crude oil- Beta	0,837	14,2	0,326

The interfacial tensions were calculated using an aqueous solution of CTAB at a CTAB concentration of 1mM.

5.1 Pore volume evolution

The Injection cell has a porosity of 25,66% and a pore opening diameter of 76 μm . The inlet droplet have an average diameter ranging from 5 to 9 μm , with the biggest droplet having a size of 30 μm . A droplet distribution of the inlets of the three model emulsions are given in the Figure 5.1.

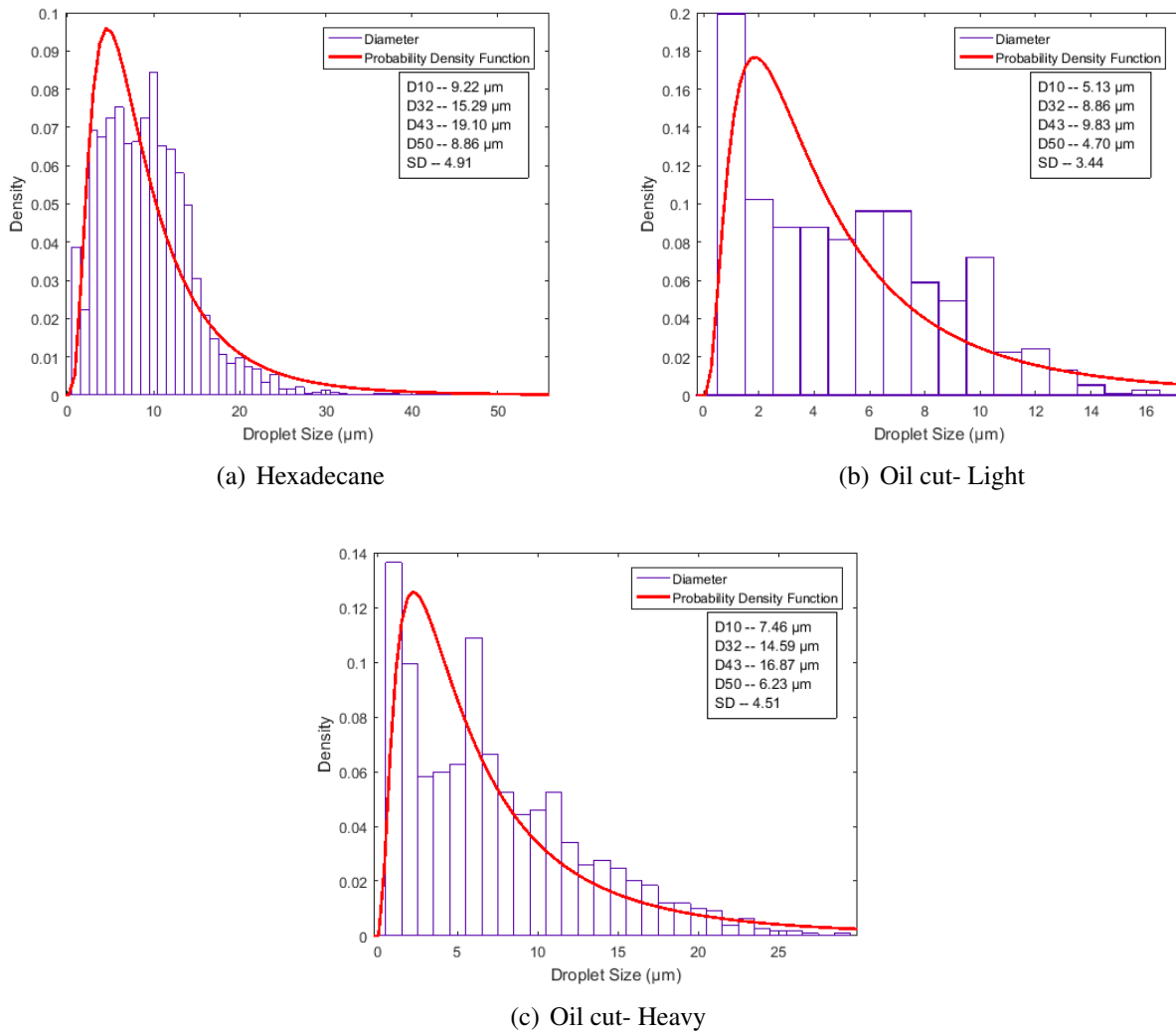


Figure 5.1: Droplet size distribution

It can be seen that the droplets are smaller compared to the pore opening. Even though same mixing speed and mixing time were used, the droplet sizes vary for the three different oils. Through out this project arithmetic mean(D10) was used as the average. It is to be noted that the three graphs are at different scales. The major reason for the difference in droplet size distribution is viscosity difference. The graph 5.2 shows the result obtained from the pore volume test of three model oil emulsions. The result obtained from the hexadecane emulsion was in agreement with the findings of Soo and Radke[44]. It can be seen that no big droplets were present after the first pore volume passing(16 pv). Then the droplet size distribution started to increase. After a while the droplet distribution came to a steady value. Not much of a difference was observed in the droplet distribution of outlets after 80 pore volume passing. Soo and Radke also reported the same effect where they observed gradual increase in permeability reduction which reached a steady value after a while. A permeability calculation was not possible in this study since no pressure drop was observed across the injection cell. The pressure at the inlet and the outlet were increased as the

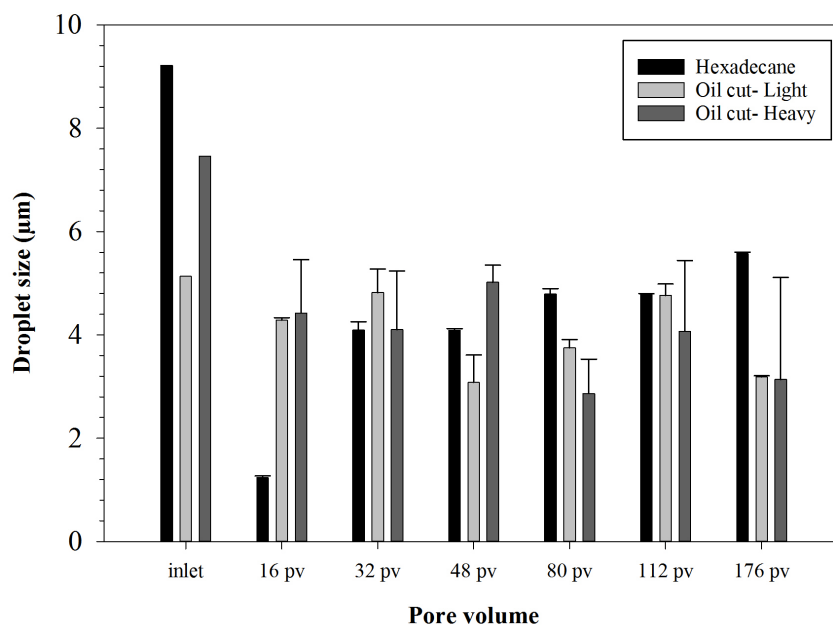


Figure 5.2: Pore volume evolution

emulsion was passed through the cell. However a significant difference in the pressure at the inlet and outlet was not observed even at the later stages of the experiment. An effort was made to analyze the change in concentration of the oil after the passing by extracting the oil from emulsion using dichloromethane. The surfactant formed a highly stable emulsion that the complete extraction was impossible. So a quantitative analysis of the concentration was not possible due to technical insufficiency. Instead, a comparative study was done assuming that the total area of the droplets observed through the microscope is directly proportional to the concentration of the oil. The graph 5.3 shows this result.

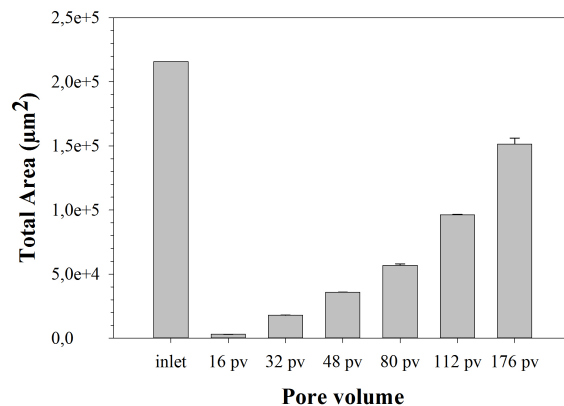


Figure 5.3: Total area evolution

As it can be seen from the graph that the concentration of the oil is increasing after every pass. This observed trend can be explained by the interaction between the droplet and the porous medium. Mechanical blocking of the droplets cannot be very significant in this case as the droplets are small compared to the pore opening. Though the probability of straining in the internal constrictions due to localized narrow paths cannot be neglected. The main mechanism has to be the interception, where the droplets were attached to the porous wall due to different chemical interactions. In the beginning, when the porous medium is free of oil, it possesses a large free surface area where the oil can be attached to. As more emulsion was being passed, more and more area became covered with oil. This caused a reduction in the capturing rate which eventually comes to zero as all the attachment sites were occupied. This could be the reason why the concentration of the oil at the outlet was low after the first sampling and gradually increased. Images of the cell after every run is shown in the Figure 5.4, where the images are arranged in the increasing order of pore volumes from the left starting from 16 pv.

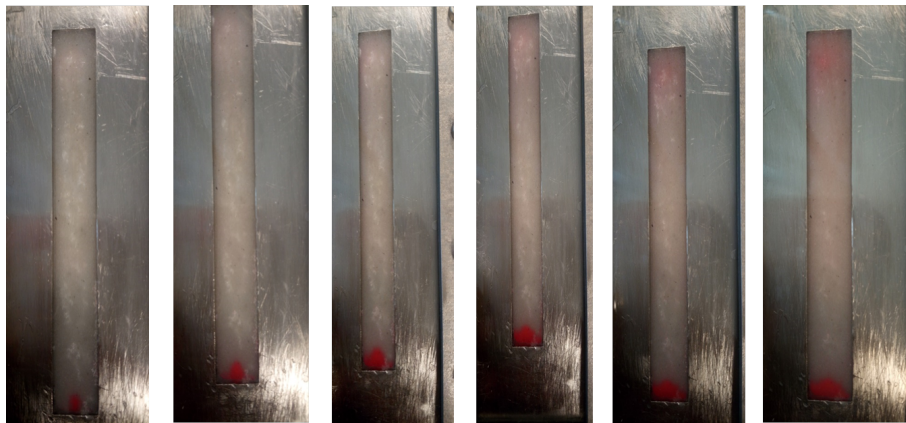


Figure 5.4: Image of cell showing oil deposition after every pass

The cell images confirm the deposition of the oil droplets inside the porous medium. The oil droplet can be seen as the pink colour in the cell due to the presence of the dye.

Such a trend was not visible in the case of the two crude oil distillate cuts. It can be seen that the inlet average size is smaller for the light oil cut and it could be the reason for the observed high average droplet size after the first passing. But the droplet sizes of the heavy cut are comparable to that of hexadecane. Yet the outlet had more bigger droplets for the crude oil cut. This also explains the importance of interaction between the oil and the porous wall. It is possible that water was preferably wetting the surface than the oil which prevented the oil from getting attached to the glass beads[51]. More droplets passed through the porous cell without being captured as it was less wetting. Other chemical properties were also could be a reason for the absence of interaction between the wall and the droplets. It is interesting to note that even when the interception was not significant, there was still some deposition suggesting that some level of straining is taking place inside the cell even when the droplets are smaller than the pore opening.

5.2 Effect of flow rate

The graph 5.5 shows the result obtained from the flow rate test conducted using hexadecane as the dispersed phase.

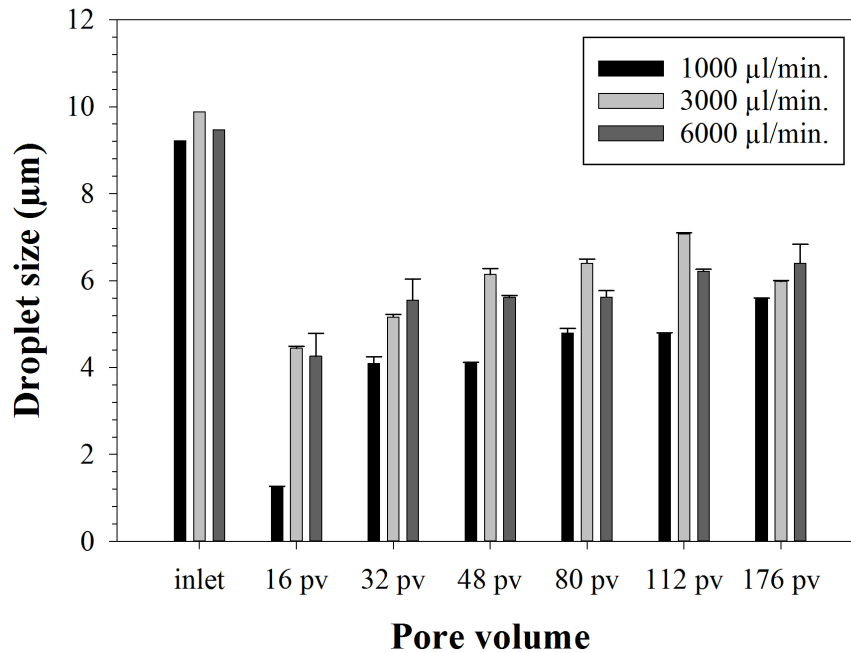


Figure 5.5: Effect of flow rate on emulsion transport- Hexadecane

It can be seen that the average droplet size increased as the the flow rate increased. The superficial velocities were 0,022 cm/s, 0,066 cm/s, and 0,132 cm/s. As discussed in the theory section, the forces responsible for droplet attachment are the surface forces and the hydrodynamic forces. Drag force has an important role in droplet attachment. As the superficial velocity increases, drag force also increases which results in detachment of the droplets from the wall surface if the drag force overcomes the attractive forces. It can be seen that the outlet droplet size distribution increased drastically as the flow rate increased suggesting that the high flow rate resulted in decreased attachment rate. Previous studies done on the effect of velocity[54] also suggested that the high flow rate will result in the squeezing of the already captured droplets by the mechanism of straining causing the re-mobilization of the droplets. So it can be assumed that both the interception as well as the straining mechanisms were affected by the flow rate. Hence most of the bigger droplets travelled through the cell without being captured by the wall.

Such an effect was not visible in the case of the two oil emulsions. Not much of a difference in the average droplet size distribution was observed in the earlier injections. The results are given in the graph 5.6.

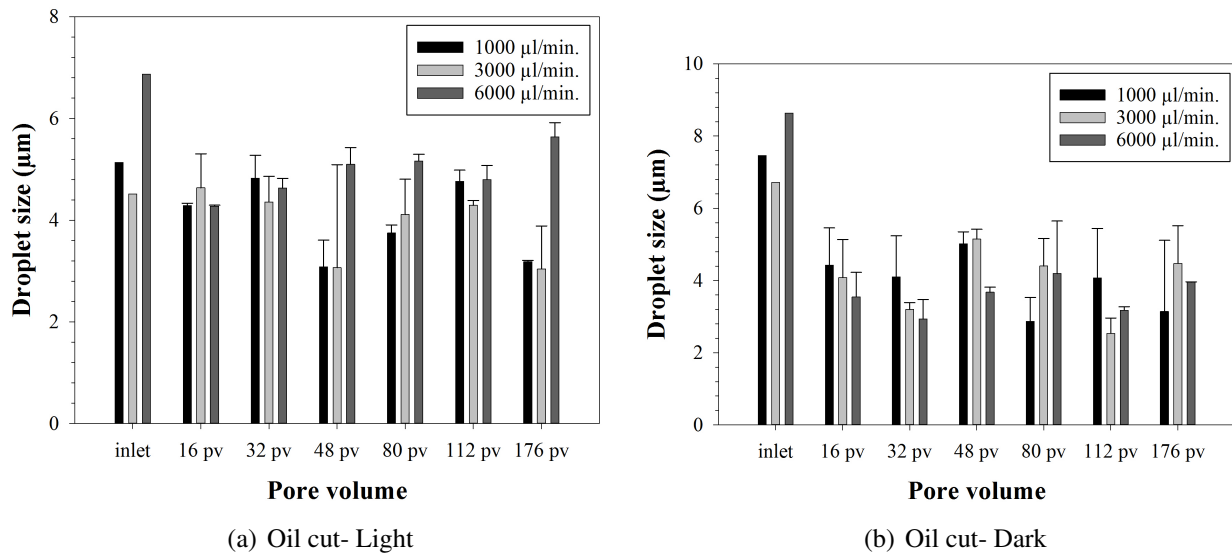


Figure 5.6: Effect of flow rate- Oils

It has already been seen that the oils have lower adhesion to the glass walls. Since the interactions are less for oils, only the large droplets might have captured by straining and only droplets with very high attractive force towards the glass wall get captured by interception. These droplets were not affected by the drag force. It can be noted that the average size distribution started to increase in case of the light oil at the higher pore volume injections. It suggests that some of the captured droplets were actually re-mobilized, but might have taken longer time to make their way to the outlet.

5.3 Effect of bead size

The table 5.2 shows the size of the different beads used and the respective porosity and the average pore sizes.

Table 5.2: Porosity and Average pore size data

Bead size(μm)	Porosity	Pore size(μm)
150- 212	25,66%	75
425- 600	26,83%	212,28
710- 1180	28,33%	391,4

Both porosity and the pore size increased with the bead size. The graph 5.7 shows the result obtained from the bead size experiments conducted with hexadecane.

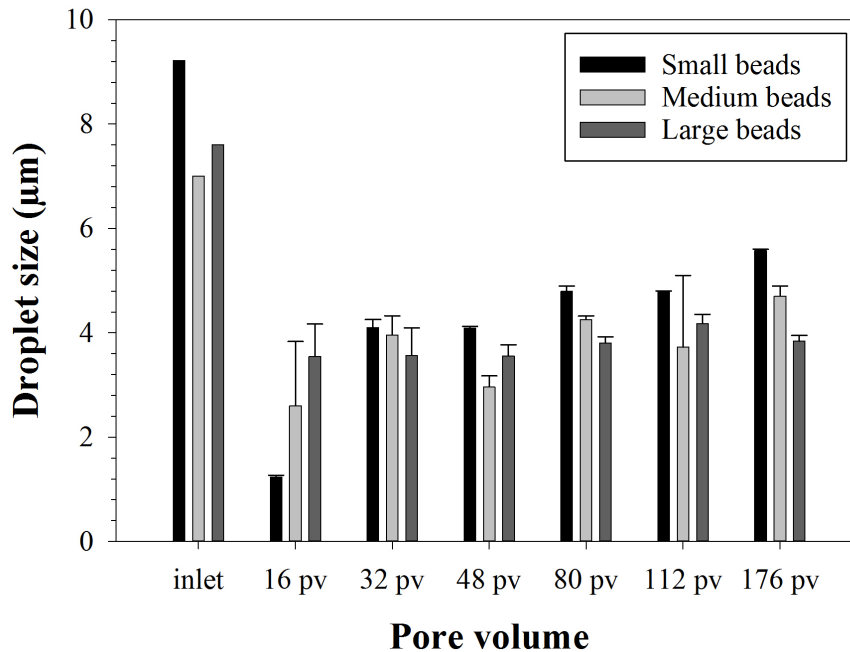


Figure 5.7: Effect of bead size on emulsion transport- Hexadecane

After the 16 pore volume injection, it was observed that the outlet droplet size was higher for the biggest glass beads which had the highest porosity and average pore size. But the trend did not continue after that. From 32 pore volume on wards it has been seen that the outlet had similar or smaller droplets compared to the small bead packing. The increase in bead size had no effect on the outlet droplet size distribution. The increase in the droplet size after the first injection can be explained on the basis of surface forces. For the attachment to happen, there should be sufficient attractive force between the droplet and the glass bead. It has already been discussed in the theory section that the attractive forces are stronger at small distances. When the beads were bigger, it created a bigger pore size. Since the droplet had enough space to flow, very few droplets reached close enough to the wall for an attachment to occur. It is also true in the case of straining. When the pore size increases the chance of droplets getting trapped in the constrictions decreases. These reasons resulted in an increase in outlet droplet size distribution as the bead size increased. It has been observed a high creaming as the time passed, which prevented the bigger droplets from entering the outlet stream. The droplets had enough vertical space to cream to the top and they stayed on the surface and did not enter the outlet stream. The Figure 5.8 shows the picture of the cell after the creaming occurred.



Figure 5.8: Creaming due to high porosity of the cell

So the observed decrease in droplet size is not because of the capturing of the droplets inside the cell, but because of the creaming of the droplets. Graph 5.9 shows the result obtained from the test using crude oil cut-light.

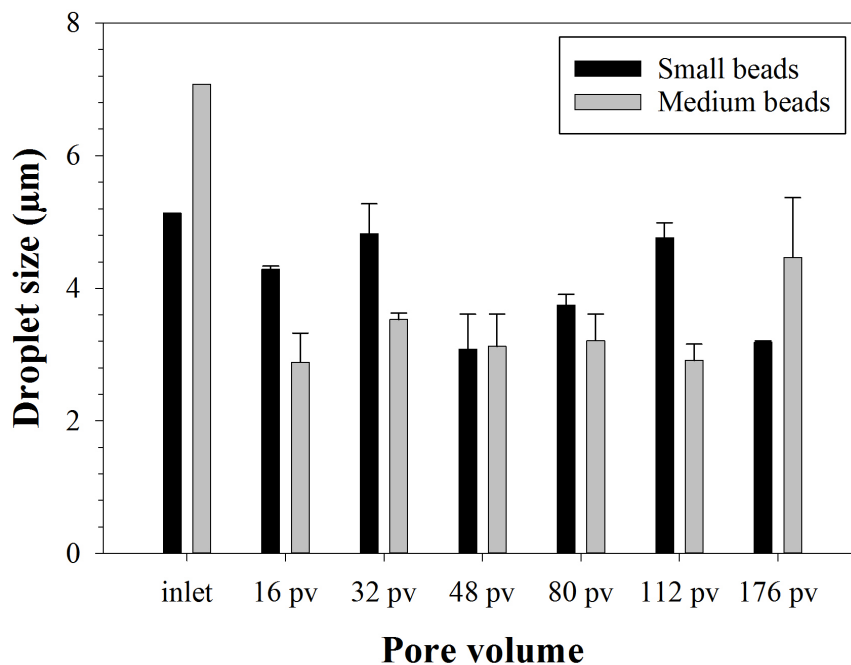


Figure 5.9: Effect of bead size- Crude oil cut

The oil sample also showed a similar trend confirming that the entrapment of dispersed phase

inside the porous medium decreases as the size of the packing material, which means the porosity, increases. A test with the biggest beads was not done for the oil since it was already high creaming with the medium beads.

5.4 Droplet size test

The Figure 5.10 shows the three droplet sizes used for the hexadecane and the crude oil cuts. Even though the same speed and time of mixing were used while making the colloids with three kind of dispersed phases, it resulted in three different droplet size distribution due to the different viscosity of the three oils. The main idea of this test was to study the effect of droplet size on emulsion transport.

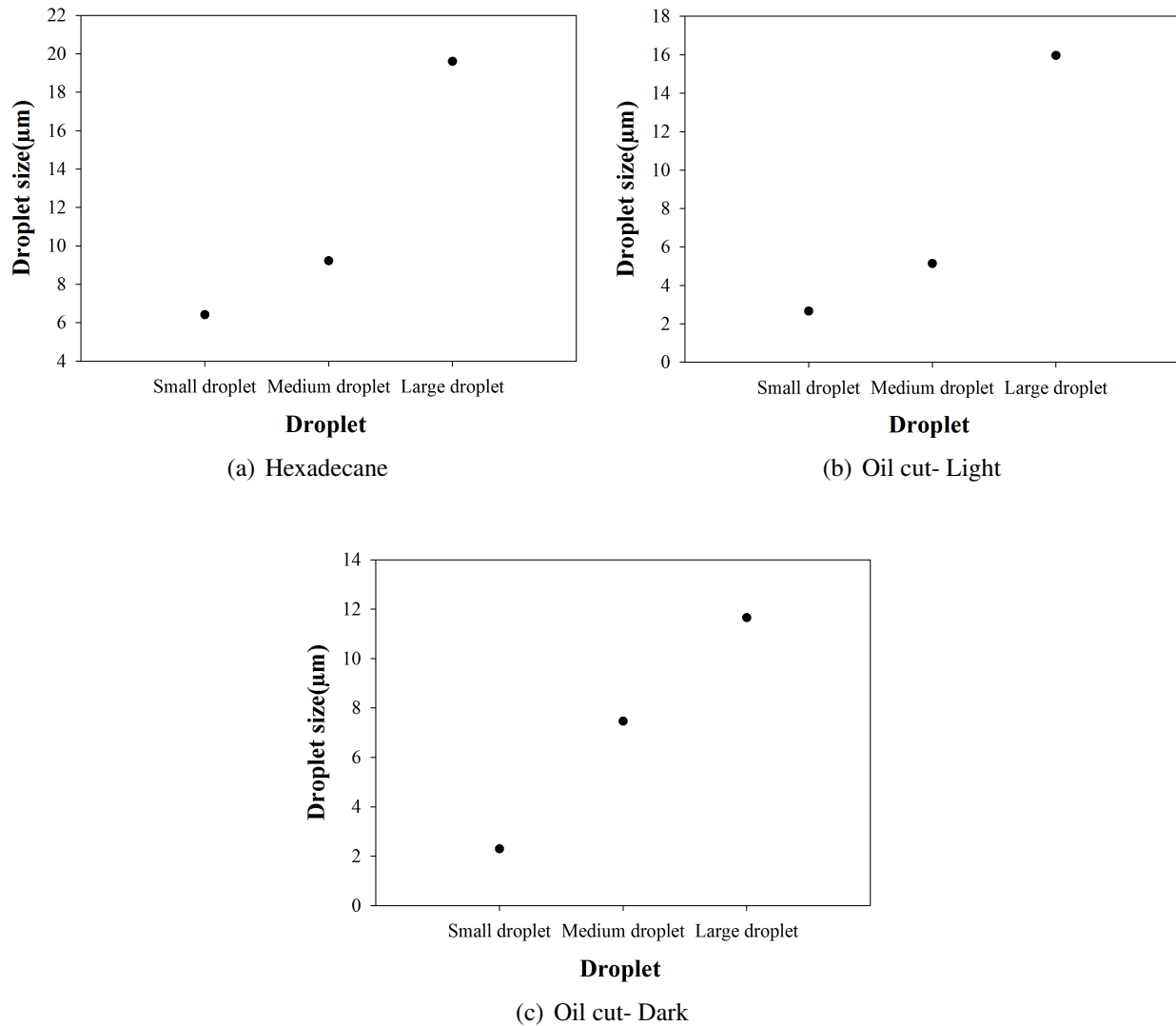


Figure 5.10: Average droplet sizes

The result obtained from the droplet size test are given in the Figure 5.11. It should be noted that the outlet average droplet sizes were reported as a fraction of inlets. It will help in understanding the effect in a clear sense as the inlet droplet sizes are also different. So for each test the outlet droplet sizes were divided by the corresponding inlet droplet sizes.

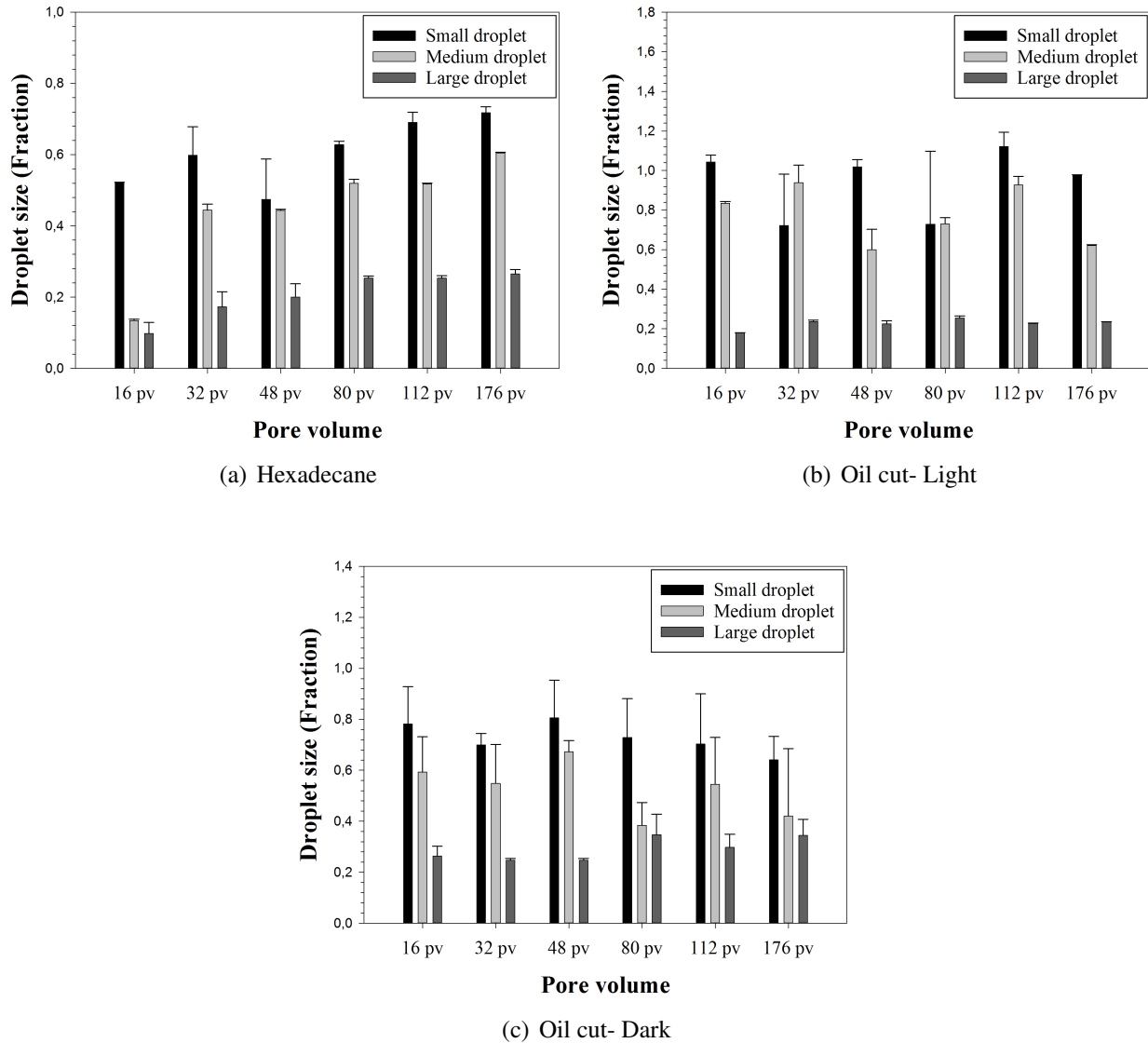


Figure 5.11: Droplet size test results

It can be seen that after 16 pore volume injection almost 60% of the inlet average droplet size was obtained in the outlet in the case of small droplet size of around $6 \mu\text{m}$, where only 15% of the initial droplet size was observed in the outlet for the largest droplets. A gradual increase in the droplet size can be seen as the pore volume injection increases, similar to the effect observed in the pore volume evolution test. In the case of crude oil cut- light, almost the same average droplet size

was observed at the outlet after 16 pore volume injection for the smallest droplets which had an average size of around $2\ \mu\text{m}$ only. Crude oil cut- light also showed the same trend of less deposition of oil droplets in the cell for the small droplet size for all the pore volume injections. The heavy oil cut also showed the same trend where around 80% of the inlet size was recovered in the outlet after 16 pore volume injection for the small droplets where for the large droplet it was only 22%. This result can be compared to the one obtained in bead size test. In this case also the parameter which changed was the droplet size to pore size ratio. Since the pore size was constant, the smallest droplets gave the smallest ratio and which resulted in a high fraction of inlet size in the outlet. As discussed earlier, the distance between the droplet and the wall is important in surface forces. So when the droplet size to pore size ratio decreases, the chance of droplets getting close to the glass wall so that the attraction can be significant to cause an attachment of the droplet decreases. Hence most of the droplets travelled through the cell without being captured by the wall in case of small droplet sizes. The straining will also be less for smaller droplets as the pore constrictions became big enough for the droplets to pass through. A picture of the cell for the test with the light oil cut also agrees to this observation, which is shown in the Figure 5.12



Figure 5.12: Cell image showing the deposition of oil

Very negligible deposition can be seen for the test with the small droplet size.

5.5 Salinity test

The Figure 5.13 shows the change in interfacial tension according to the continuous phase. All the continuous phases contain CTAB addition to the components mentioned in the table.

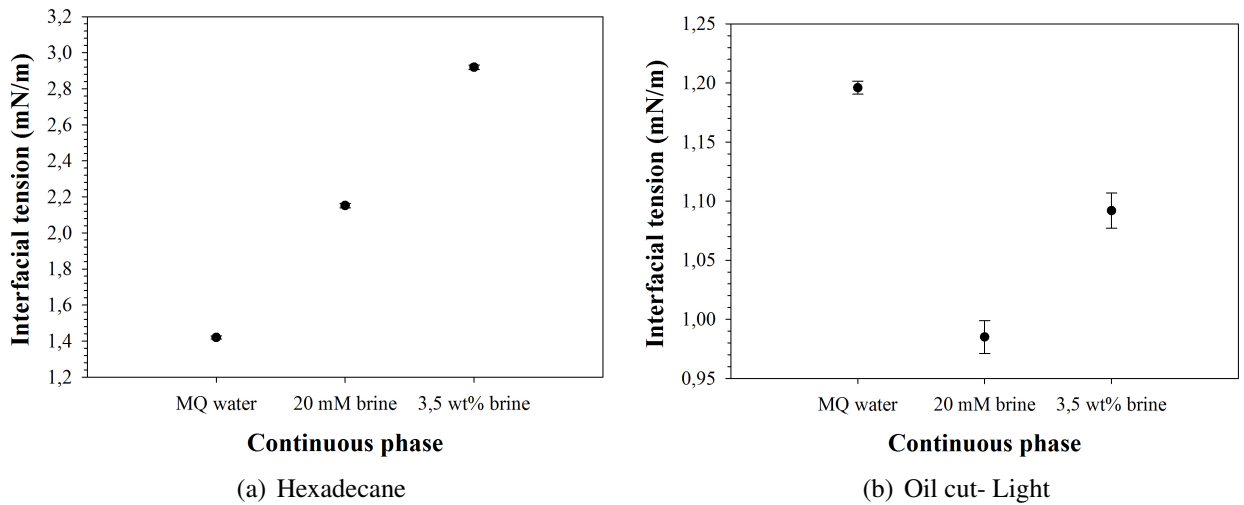


Figure 5.13: Interfacial tension data for different salt concentrations

An increase in the the interfacial tension was observed in the case of hexadecane. The observation was different for the light oil cut. The interfacial tension decreased for 20 mM brine solution compared to the MQ water. But further addition of the salt resulted in an increase in the value of interfacial tension. The reason for the different responses for the two oils lies in the surface chemistry and the chemical species present. It is not discussed in this project as it is out of the scope of this project. So the values are just reported here. The Figure 5.14 shows the results obtained from the salinity test for hexadecane and the crude oil light cut.

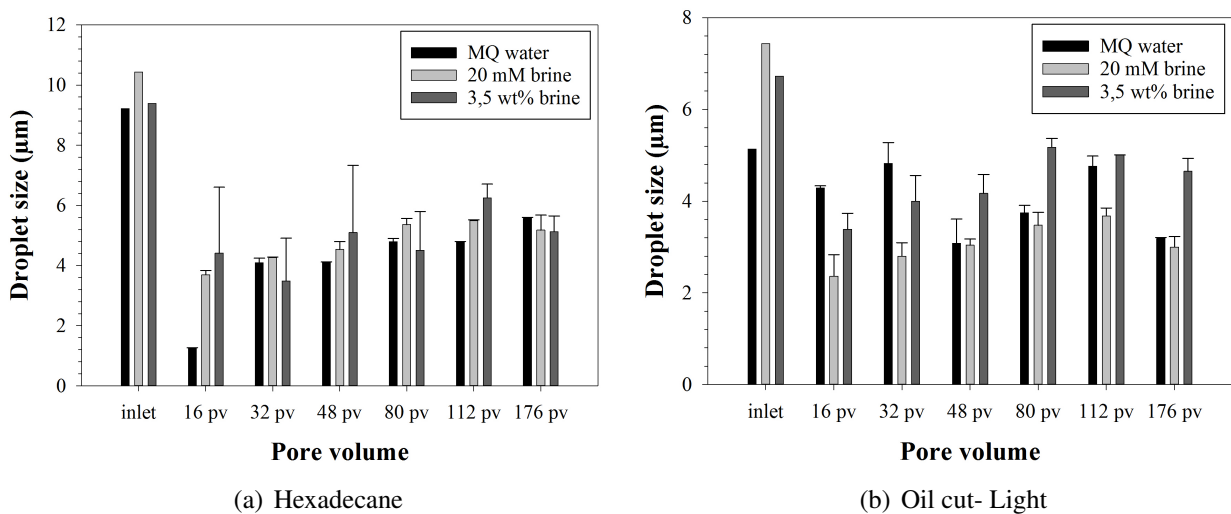


Figure 5.14: Effect of salinity on the emulsion transport

For hexadecane, an increase in the outlet average droplet size was observed as the salinity

increased. This means that the adhesion of the droplets to the glass beads decreased as the salinity of the continuous phase increased. Towards the last pore volume all three emulsions gave almost the same outlet size. It can be assumed that it was the equilibrium droplet size after passing. But in the case of light oil, the trend was different. It can be observed that the droplet size decreased for 20 mM brine and again increased for 3,5 wt% brine. This means that the interaction between the oil droplets and the glass beads increased for 20mM brine compared to the MQ water and again decreased for the 3,5 wt% brine.

There are two possible explanations for this observed result. First one is based on the wettability of the dispersed phase. As we discussed in the pore evolution section, preferential wetting of the surface is important for the attachment of the droplets. It could be assumed that the salt content decreased the wettability of hexadecane and in case of crude oil light cut, it first increased the wettability at low salinity and again decreased it as the salt concentration increased. A wettability study is required to confirm this hypothesis. Another approach is based on the interfacial tension. J.A.M.H Hofman and H.N Stein[43] conducted similar studies and reported the effect of interfacial tension in droplet attachment. As per their studies, when the interfacial tension is lower, the droplets require less energy to reform itself into the shape of the material to which it is getting attached to. This can be seen in this experiment too. For hexadecane, interfacial tension increased along with the salt content. This also resulted in less deposition of the oil droplets to the glass beads. When the interfacial tension is high, the surface energy was not sufficient to cause a reformation and hence attachment was difficult. This is also true in the case of light oil cut. The 20 mM brine solution has the lowest interfacial tension, which resulted in the highest deposition of the droplets in the cell. So it can be assumed that the reduction in interfacial tension caused the oil droplets to adapt the shape of the glass beads easily which lead to a better attraction between them.

5.6 Test with crude oil

The Figure 5.15 shows the result obtained from the pore volume test done with crude oil.

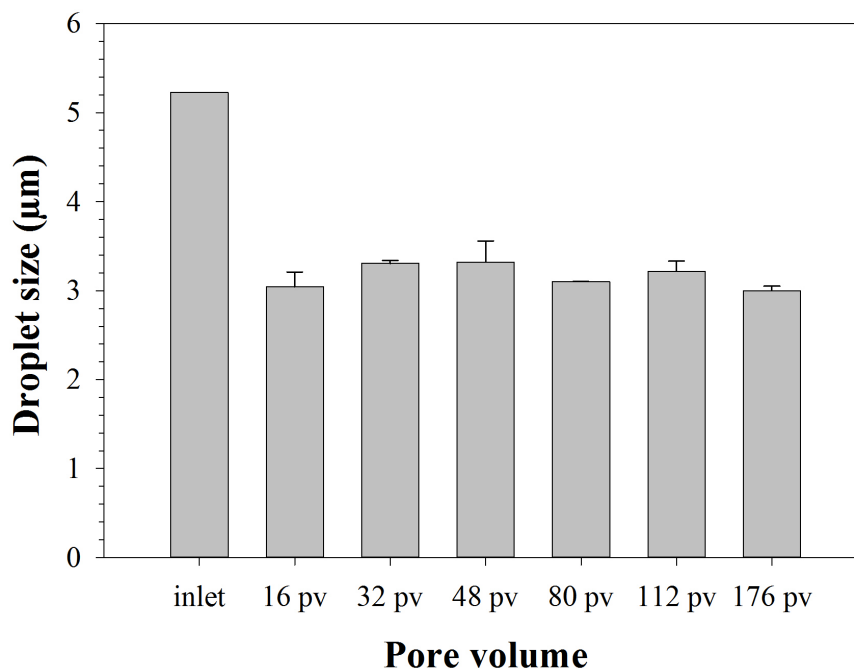


Figure 5.15: Pore volume analysis for Crude oil- Beta

It showed similar trend as the crude oil distillate cuts. No significant interaction between the droplets and the glass beads were observable. All the pore volume injections resulted in same outlet droplet size distribution. Further more no deposition of oil in the cell was also visible. The figure 5.16 shows the change in interfacial tension values according to the change in the continuous phase salinity. Results obtained from the salinity test with crude oil is given in the Figure 5.17.

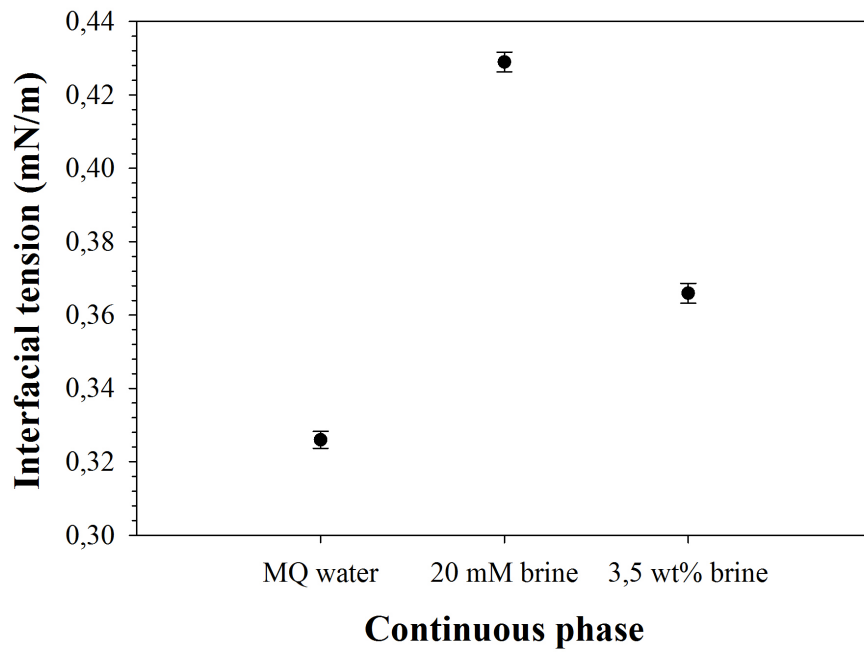


Figure 5.16: IFT data for crude oil at different salt concentrations

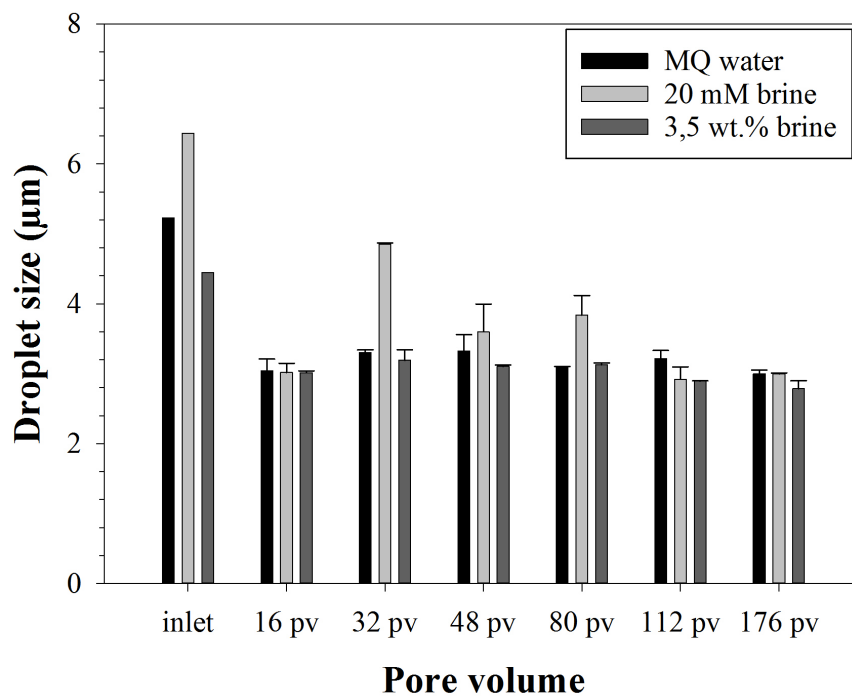


Figure 5.17: Salinity test- Crude oil (Beta)

The interfacial tension was observed to be increased for 20 mM brine compared to MQ water and then decreased for 3,5 wt% brine solution. It was a trend opposite to that observed on the case of crude oil distillate cut. A corresponding trend in the outlet droplet distribution was not visible where an expected increase in deposition for lower interfacial tension and vice versa. In most of the pore volumes all three emulsions showed a similar outlet droplet distribution suggesting the continuous phase salinity did not affect the interaction between the droplets and the glass beads. This suggests that the interfacial tension alone is not sufficient to cause a change in the interactions. The presence of other components and the surface chemistry of the oil are important in surface interactions. Compared to the other model oils used in this project, the crude oil contains inherent surface active agents such as asphaltenes and resins. The presence of heteroatoms and metals also affect the surface chemistry of the crude oil. So all these components contribute to the surface interactions of the crude oil and a detailed study of this components are required to understand the interaction of crude oil with porous medium.

5.7 Advantages of the methodology used in this project

Most of the studies done on the transport of emulsion through porous medium were core flooding experiments. In this project a different experimental setup was used, where a purpose built cell was used for the studies. From the above analysis it can be seen that some of the results obtained in core flooding experiments were reproduced using the cell. This proves that the cell provides similar environment as the core flooding setup. Compared to core flooding, the cell has the following advantages.

First of all it was easy to handle the setup as the size was smaller compared to the core flooding experiments. The loading and unloading of the packing material was also easy and the cleaning of the packing material as well as the cell was less time-consuming. Further more, the surface properties of the packing medium is easy to alter by functionalization of the glass beads. A main advantage of this methodology was that a real time observation of the process happening inside the cell was possible through the glass window. A better understanding of whether the deposition was due to attachment or due to creaming was possible by this method. Also the alteration of the porosity of the cell is possible by using different size glass beads. This project was hoping to give a better understanding of the attachment phenomena by analyzing the cell under microscope. Due to the technical issues, it was difficult to capture the pictures using the microscope. Some of the images taken using the microscope are given in the *Appendix A.2*. But with the right fluorescent dye it will be possible to capture the pictures which shows the state and shape of the droplets captured by the porous medium. Such an analysis will have huge advantage for this method over the classic core flooding method.

Conclusion

1. The pore volume experiments showed that the main mechanisms of droplets capture inside the porous medium are straining and interception, which agrees to the deep bed filtration model of emulsion transport.
2. The surface properties of the dispersed phase are important in the interaction between the droplets and the porous wall. The wettability of the dispersed phase is one such important property.
3. The flow rate of the emulsion has an effect on the droplet capture. As the flow rate increases, drag force increases which cause a reduction in the attachment rate. Further more the flow rate affect the straining also as the already strained droplets can be squeezed at the high flow rate causing the re-mobilization of the droplets.
4. The droplet size to pore size ratio is important in droplet capturing. When the droplet size to pore size ratio is very small, the droplets will not come close enough to the wall where an attractive force can be significant.
5. The salinity has an effect on the interfacial tension of the oil. This change in interfacial tension affects the emulsion transport. When the interfacial tension is lower, the droplets deform at a very low surface energy which in turn increases the capture of the droplets by the porous wall.
6. The methodology used in this project was showed to have the advantages over core flooding such as easiness of handling and cleaning. Easy to change the porosity and finally enables the visual observation of the droplets inside the cell.

Future work

A measurement of the concentration of the oil in the outlet was not done in this project due to the difficulty of extraction of the oil from the emulsion. So the UV-Vis method cannot be used to measure the concentration. Some other methods such as carbon assay can be used to measure the concentration. The concentration measurement will give a more quantitative results about the amount of oil being captured and the time taken to reach the equilibrium state where the outlet has the same concentration as the inlet. The main idea of this method was to analyze the cell under microscope. It was not done due to the technical difficulty. By loading the oil with a water insoluble fluorescent dye will help to see the oil droplets captured in the cell under a fluorescent microscope. Such a dye and the loading method need to be studied further. The produced water contains suspended solids in it. By introducing solid particles in the emulsion, a more realistic study of the produced water transport through porous media can be understood.

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Appendices

A.1 Porosity calculation

Weight of the glass beads was calculated by measuring the weight of the cell before and after filling the beads.

$$\text{Weight of cell without beads} = 1186g \quad (\text{A.1})$$

$$\text{Weight of cell after filling the beads} = 1196,7 \quad (\text{A.2})$$

$$\text{Weight of glass beads} = 1196,7 - 1186 = 10,7 \quad (\text{A.3})$$

$$\text{Density of the glass beads} = 2,4g/cm^3 \quad (\text{A.4})$$

$$\text{Volume of glass beads} = 10,7/2,4 = 4,46cm^3 \quad (\text{A.5})$$

$$\text{Total volume of the cell} = 8 * 1,5 * 0,5 = 6cm^3 \quad (\text{A.6})$$

$$\text{Void volume} = 6 - 4,46 = 1,54 \quad (\text{A.7})$$

$$\text{Porosity} = 1,54/6 = 0,2566 \quad (\text{A.8})$$

Therefore the porosity of the cell when the glass beads of 150- 212 μm diameter were used is 25,66%

A.2 Cell images taken with microscope

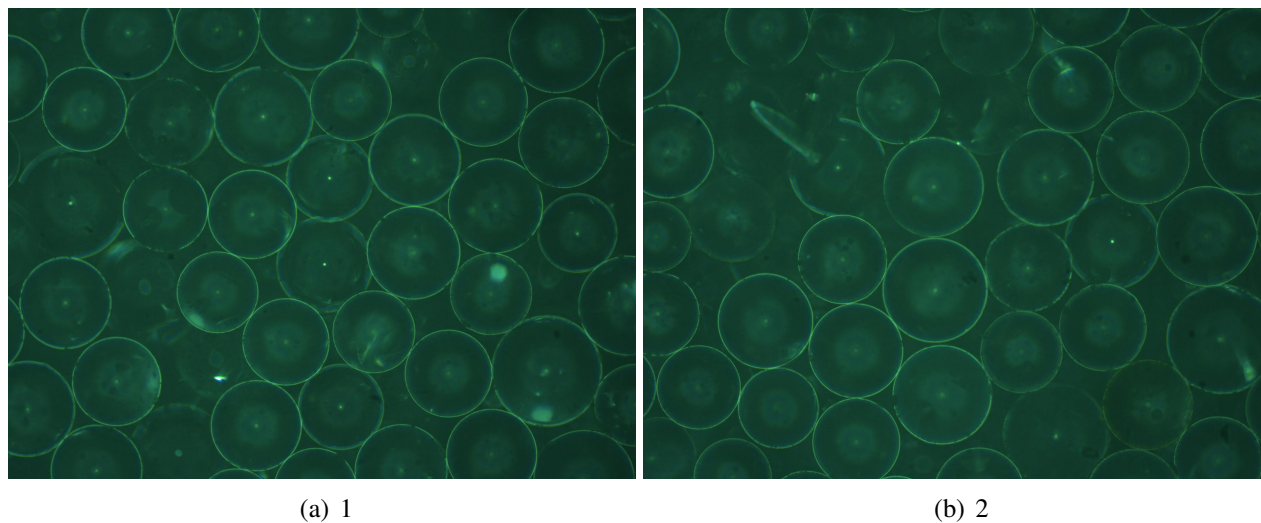


Figure A.1: Image of the cell with beads before emulsion passing

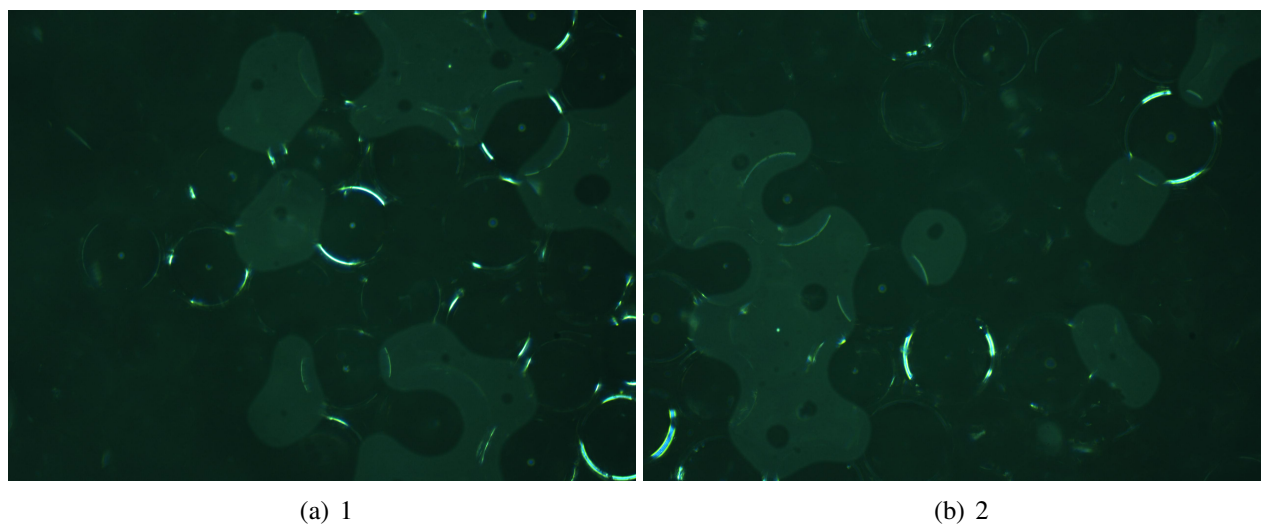
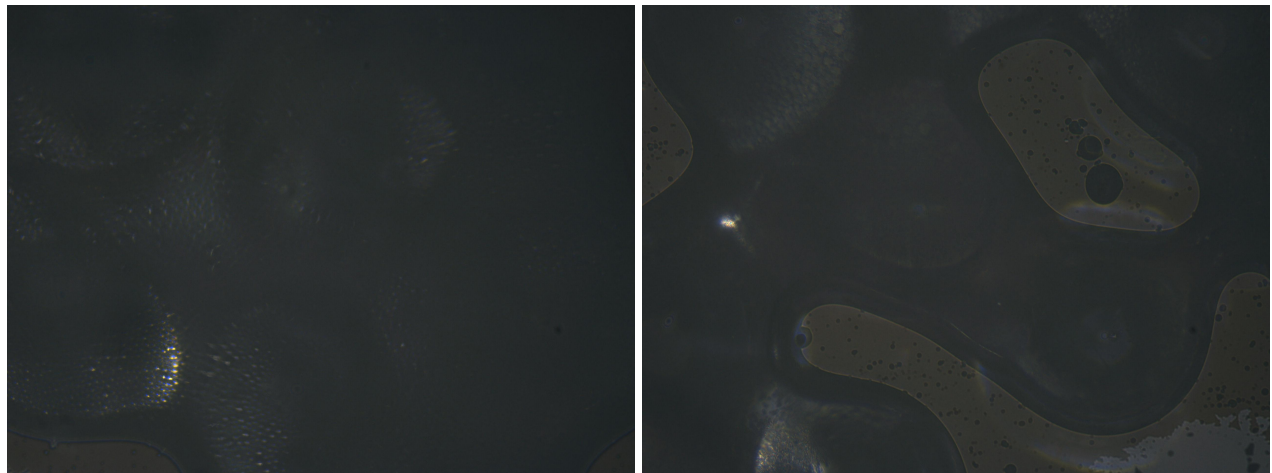
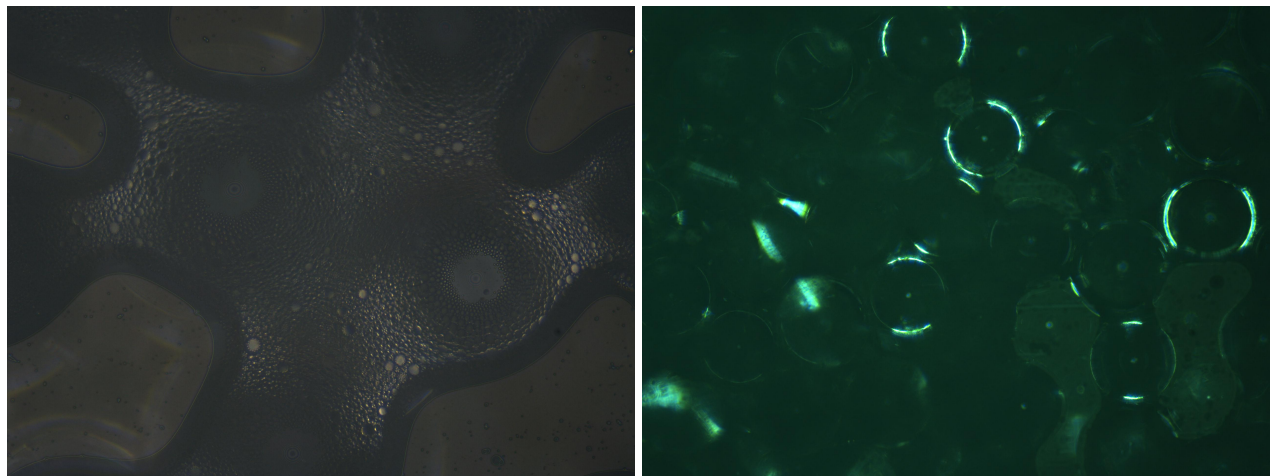


Figure A.2: Image of the cell with beads after water passing



(a) 1

(b) 2



(c) 3

(d) 4

Figure A.3: Image of the cell with beads after emulsion passing