Iraqi Journal of Chemical and Petroleum Engineering
Vol.17 No.3 (September 2016) 11- 31
ISSN: 1997-4884

Iraqi Journal of Chemical and Petroleum Engineering

University of Baghdad
College of Engineering

Using Different Surfactants to Increase Oil Recovery of Rumaila Field (Experimental Work)

Talib A. Salih, Safaa Hussain Sahi and Ahmed Noori Ghani AL-Dujaili
Petroleum Engineering Department, College of Engineering, University of Baghdad

Abstract

Enhanced oil recovery is used in many mature oil reservoirs to increase the oil recovery factor. Surfactant flooding has recently gained interest again. To create micro emulsions at the interface between crude oil and water, surfactant flooding is the injection of surfactants (and co-surfactants) into the reservoir, thus achieving very low interfacial tension, which consequently assists mobilize the trapped oil.

In this study a flooding system, which has been manufactured and described at high pressure. The flooding processes included oil, water and surfactants. 15 core holders has been prepared at first stage of the experiment and filled with washed sand grains 80-500 μm and then packing the sand to obtain sand packs samples for experiment. It was found that the best rate for water injection was 1.2 PV. Productively, while the optimum injection rate was 1.0 PV economically.

The study observed that the cost of water injection in secondary recovery increased 700% when PV injected increased from 1.0 PV to 8.0 PV, while the recovery increased only about 8% (58.77 – 66.7%).

The effects of concentration, salinity and temperature is also explored by examined many values of each parameter according to surface tension by using capillary rise method. It was found that the optimum conditions for surfactant flooding for sodium dodecyl sulfate (SDS) 0.01 molar for concentration, 5500 P.P.M for salinity and 70 °C for temperatures. These conditions was used to all kinds of surfactants that have been used in this study.

The study results indicated that the best surfactant in both productively and economically was SDS with maximum recovery about 90% for each secondary and tertiary recovery and the optimum injection volume for all surfactants 1.2 PV .

Another 12 Core holders with fixed pore volume were prepared for the second stage of the experiment. At this stage the pore volume was approximately constant and the variation included different values of SDS concentrations (0.1 and 0.001 Molar) and different values of salinity (1000 P.P.M and 3000 P.P.M) and temperature equal to 90 °C. Each value for concentration was experimented with the two values of salinity which in result obtaining four flooding conditions. Each condition was flooded by three injection rates (50, 120, 200 %). The results proved the results obtained from the first stage.

Introduction

The Department of Energy U.S.A, specified the amount of oil produced worldwide is one third of the total oil available only. So, by using the EOR techniques will be able to produce more oil as the demand increase while we have a shortage in the supply. Over the last three decades a lot of research was took place in the field of enhanced oil recovery and since the EOR methods have been developing. These techniques were applied on mature and depleted reservoirs and showed improved efficiency compared with primary and secondary recovery (water-flooding) [1].

Water flooding method, started after First, 1964 published his patent to increase oil recovery [2]. US. ‘Patent No. 3,302,713, discloses a surfactant which radically improves the economics of the surfactant water flooding process [3]. While the surfactant of [Ahearn et al. 1967] has been shown to be an economical and effective means for petroleum recovery, it has been found to be susceptible to depletion within the formation as are most surfactants and particularly the sulfonate surfactants [4].

Surface-active agents or “surfactants” have been proposed for addition to flood water for lowering interfacial tension between the water and the reservoir oil, thereby that’s will lead to increase the recovery of oil displaced by a water flooding. Typical surfactants which have been selected for enhanced oil recovery include alkyl pyridium salts, sodium lauryl sulfate, certain sulfonates, glycosides, sodium Oleate, and quaternary ammonia salts [5]. Nowadays many mature reservoirs under water flood have decreasing production rates despite having 50-75 % of the original oil left in the reservoir. In such cases the surfactant flooding can increase the economic productivity [6].

As mentioned before , surfactants are added to decrease the interfacial tension (IFT) between oil and water. Co-surfactants are blended into the liquid surfactant solution in order to improve the properties of the surfactant solution. The co-surfactant either serves as a promoter or as an active agent in the blended surfactant solution to provide optimal conditions with respect to temperature, pressure and salinity. Due to certain physical characteristics of the reservoir, such as adsorption to the rock and trapping of the fluid in the pore structure, considerable losses of the surfactant may occur [7,1].

Surfactant flooding is one of the three main chemical flooding processes which include polymer flooding, surfactant–polymer flooding and alkaline– surfactant–polymer (ASP) flooding. Addition of surfactant to the polymer formulation may, under very specific circumstances, reduce oil-water interfacial tension to almost zero displacing trapped residual oil [8]. The results of the core floods for Iglauer et al. (2010) [9] which indicated a good oil recovery by surfactant flooding even at high salinities. Pawga et al. (2010) [10] made a comparative study of different EOR methods to estimate the best method economically. Different EOR methods have been studied and understood as a technical part of EiT Norne Village. Gholamzadeh et al. (2012) [11] discussed Surfactant injection method in an oil-wet, dual-porosity model , concluded that the injection might not be effective. Liang Xu (2013) [12] research found that capillary pressure inside pore spaces, was not straightforward to predict or correlated to the performance of the surfactant that to be used during fracturing. Ma, (2013) [13] provided an in depth understanding of transport of surfactant and foam through porous media using a combination of laboratory experiments and numerical simulations. In conclusion, thesis provides new findings in surfactant adsorption onto mineral surfaces, in the methodology to estimate foam parameters for reservoir simulation, and in micro-model observations of foam flow through porous media. Habibi et al. (2014) [14] investigated the effect of different aging time and temperature on wettability alteration with exact soaking time in order to find the optimum condition. Iglauer et al. (2014) [15] imaged a sandstone plug at connate water saturation, residual water flood saturation, surfactant flood saturation and polymer flood saturation in 3D at high resolution micrometer level, found that the water flood was quite efficient in terms of oil recovery and the polymer flood as well.

Nguyen et al. (2014) [16] presented a comprehensive evaluation of phase behaviors of alkaline / surfactant / polymer (ASP) systems. The experimental results proved that the phase behavior of mixed-surfactant solutions (single- and double-tail anionic surfactants) would be better than the one of single surfactant. These mixtures were also more compatible with polymer, and adjusted optimum salinity to the reservoir brine. They next examined the role of alkalis in ASP process. The study showed that sodium metaborate is the best choice.

Sun et al. (2014) [17] showed that 0.4 wt% IOS2024 with 1 wt% IAA can provide ultra-low IFT of 10^{-3} mN/m at around 3000–4000 mg/L total dissolved solids, but at that salinity range the surfactant retention is very high. The search for an optimum surfactant formulation has to consider solution properties and retention in addition to the low IFT.

The following points are investigated in this work:

1. Identify the properties of sand packs which will use in the experiment by the calculation bulk and pore volume , porosity and permeability .
2. Study of the chemical reactions, which cause the loss of surfactant and the determination of the effect of water salinity (formation water) on its behavior, required the knowledge of the physical and chemical properties of the surfactant.
3. Study of all factors and properties that effected on oil recovery which includes pore volume of the injected water for secondary recovery and surfactant for tertiary recovery and the effect of surfactant concentration, salinity and temperatures on surface tension values.
4. Study of the effect of different displacement processes (water and surfactant flooding) under reservoir conditions (pressure and temperature).
5. Check the best conditions for secondary recovery and EOR which will effect on oil recovery (Concentration, salinity and temperature).
6. Identification of the production and economical limit of the injection process.
7. Comparison of three kinds of surfactant (anionic, nonionic and cationic) in both economically and productively to select best surfactant kind in EOR process in Rumaila field.

Experimental Work

Three types of surfactants were used to increase oil recovery, there were (SDS, Criton X100 and CTAB) and the effects of concentration, salinity and temperature on the surface tension have been measured. Porosity, permeability and saturation measured also. water Flooding have been done in first stage and oil recovery factor % recorded, followed by surfactant flooding. Finally the oil recovery factor tabulated and plotted.

Materials

1. Fluids

1.1. Crude Oil

The crude oil used in the research have been taken from Rumaila reservoir in the south of Iraq and provided by Al–Dura refinery.

The physical properties of the crude oil at 30 °C was shown in Table 1 [18].

Table 1: physical properties of the crude oil at 30°C

Temp., °C	30
Specific gravity	0.879
API	29.47
Kinematic viscosity, c.st	15.314
Viscosity, c.p	13.461

1.2. Water

water used in the experiment for flooding process and preparation of surfactant solutions. Density of the water used in the study was 1 gm/ cm^3 at 30 °C and the salinity was 500 P.P.M which calculated in the laboratory of Civil Engineering and Water Resources Dept. / Kufa University.

2. Surfactant

Three types of Surfactants used in this study in different concentrations.

2.1. Anionic Surfactant

Sodium dodecyl Sulfate (SDS) produced by Alpha Chemika company [19] used as anionic surfactant. Figure 1 shows the chemical formula of this surfactant.

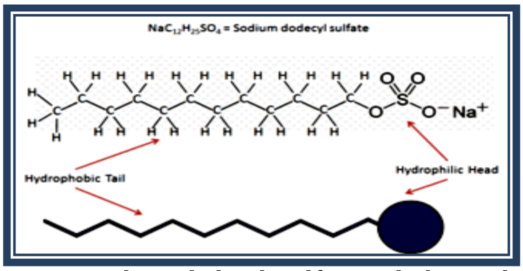

Fig. 1: Sodium dodecyl Sulfate and chemical structure

2.2. Nonionic surfactant

Poly(oxy-1,2-ethanediyl), α-[4-(1,1,3,3 tetramethylbutyl)phenyl]-ω-hydroxy-(Triton X100) produced by Central Drug House company (CDH) under trade name (Criton) [20] have been used as nonionic surfactant. Figure 2 shows the chemical formula of the Criton X 100.

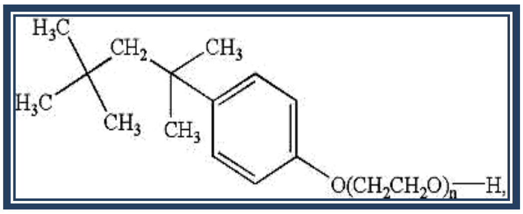

Fig. 2: chemical formula of Criton X 100

2.3. Cationic surfactants

Hexa Cetyl Trimethyl Ammonium Bromide (CTAB) produced by SCR company used as cationic surfactant. [21] Figure 3.

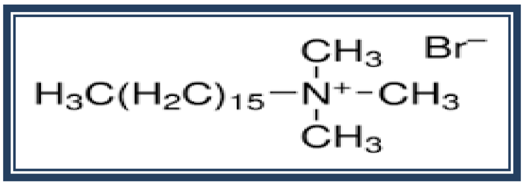

Fig. 3: chemical formula for CTAB

3. Sand

Sand has been used to prepare the sand pack with size distribution of 80 to 500 µm.

4. Salts

Sodium Chloride 99.975% has been used in the salinity experiment.

System Description

The system used in this work consists of:

1. Reservoir Tank and Accessories

Reservoir tank was made from carbon steel plates (6 mm thickness) in order to bear high pressure. This device contains also two vents , the first on the top of the tank with gate valve (inlet) to fill the tank by either water , oil or surfactant , and the second vent to ensure the filling of the tank with a reinforcement rubber pipe connected directly with high pressure CO_2 container. All the welding works were done by Argon – Tungsten in order to resist the high pressures. A schematic diagram of the part A including reservoir tank and all accessories is given in Figure 4.

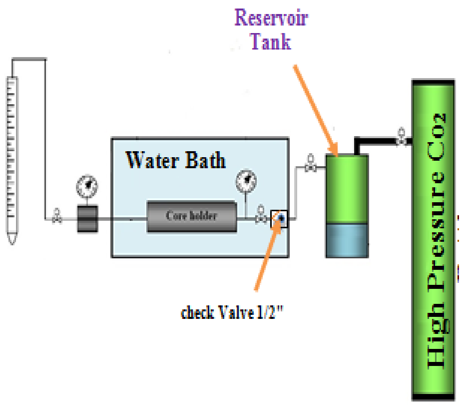

Fig. 4: Sketch Of Flooding Device

The reservoir tank also have outlet vent consist of a 1/2" pipe, check valve to keep the liquid in the desired direction and also keeping on the pressure at the required value, gate valve to close this part after all liquid was pumped. The system also provided with a pressure gage to monitoring the pressure at the desired value. The end of the reservoir tank system (Part A) was provided by 1.5" net to connect this part with the part B (sample system). Also see Figure 5.

Fig. 5: Flooding Device

2. Core Holder and Water Bath

Part B (Core Holder) consists of a double-tube high-pressure reinforcement rubber has an internal diameter of 1.5" connects with Part A according to the base of the nut with the dentate part on one hand, and with a core holder in other hand, which consists of a pipe has an external diameter of 1.5" (38 mm) and internal diameter of (30 mm), Core holder was made of anticorrosion stainless steel (grade 316) welded with pipe bushings (1.5") at the ends of the pipe. Also it provided with very fine sieve welded inside the pipe to prevent movement of sand pack or sand grains along the pipes. Figure 5 and 6.

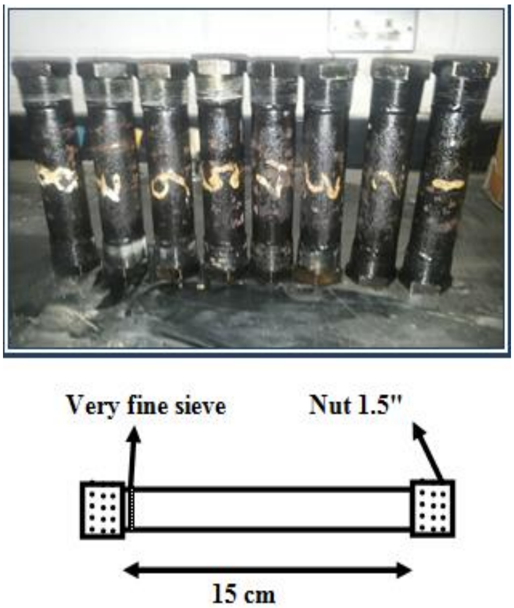

Fig. 6: Core Holders

The sample model also contain an open tank made from carbon steel gage (4 mm thickness), the dimensions of the tank (30 cm length, 20cm height and 15 cm width). The tank filled with water to use as a water bath to control the desired temperature in the experiment by providing an electric heater and thermostat.

3. Collection Section

Collection section made to connect with Sample model to receive the fluid output of the injection process, then accumulation to measure the amount of fluid that has been obtained from the injection process. Figure 4 and 5. The apparatuses used in the experiment were:

A -Fluid injection system

During the experiments a CO_2 2000 psi bottle used to displace fluids in the sand pack.

B- Check valve

Used to provide high pressure for injection. The check valve was used to move the fluid forward only and compact the contained fluid.

C- Heater

For heating the injected surfactant solution a heater placed on route. Over this heater, a vessel containing a high boiling point material have been placed.

D- Pressure differential gauge

Used to measure the pressure drop along the sand pack with 3000 psi as a maximum reading.

E- steel pipes, rubber reinforcement high pressure pipes

The design of the system made to simulate "Chemical flooding under reservoir conditions device" which is not available in Iraq in the time of the experiment. A schematic diagram of the system is given in Figure 4 and 5.

Experimental Procedure

1. Sand Pack Preparation

Silica grains with size distribution of 80 to 500 μm were used for preparing sand pack to obtain a homogeneous model with appropriate permeability. The silica's seeds strew into the core holder after washing. Screen and very tiny mesh were installed at the inlet and outlet of core holder to prevent removal of silica.

2. Sand Sieving and Cleaning

The sand was sieved and the 80-500 μm sized sand was taken for the experiments. The sand was cleaned firstly by thorough water washing to ensure removing the undesired salts. The cleaned sand was then dried.

Porosity Measurement

In this work the weight method was used to determine porosity. In this method the sand pack was measured in dry state initially, then it was saturated with water and the mass was measured again. The difference between two measured mass was equivalent to the mass of water which was saturating the sand pack. So the pore volume of saturated water can be calculated regards to water density (usually 1 gm/cm^3). With distinguishes of bulk volume, the porosity can be determined using Eq. 1 . The porosity measurements of all sand pack samples have been listed in appendix A.1.

$$Porosity = \frac{Pore\ Volume}{Bulk\ Volume} \qquad \ldots(1)$$

Permeability Measurement

The sand pack permeability was measured with oil after porosity measurement . The measurement was based on Darcy's Law which can be rearranged as the following equation :

$$\frac{q\mu}{A} = k\frac{\Delta P}{L} \qquad \ldots(2)$$

Where:

q = Flow rate in cm^3/sec

μ = Viscosity of the fluid in c.p

A = Cross-sectional area of the sand pack in cm^2

k = Permeability in Darcy
Δp = The pressure drop along the sand pack in atm.
L = Length of the sand pack in cm

The flow rate and pressure values for each sand pack which used to calculate the permeability explained in detail in Appendix A.2.
The properties of sand pack shown in Table 2.

Table 2: Sand pack overall Properties

Property (Unit)	Sand pack
Core Diameter (cm)	3
Core height (cm)	15
Bulk volume (cm^3)	106.02875
Porosity (%)	33.859 - 35.84
Permeability (m.d)	848

After the permeability has been calculated, the samples weighted again to obtain the mass of oil that saturated the sand pack. The density value was known, so the volume of oil saturated was calculated also as in Appendix A.3.

Emulsion Preparation

The emulsion was prepared in (1000 ml) glass prescription bottles.

Core Flooding Experiments

Experiments have been carried out on a conventional sand pack and in the following orders:
1. Crude Oil Flooding
After sand pack preparations, the oil saturated sand pack at presence of irreducible water under variable conditions of flow rates and pressures (Temperature was constant at room temperature).
First, twelve experiments have been done then core holder for each experiment weighted to calculate the mass of oil in the sand pack, because the density of the oil known (Table 2), so it's volume was calculated for each sample as in the Appendix A.3.

All parts of the system and beakers were cleaned by detergent and water and dried by compressed air after any stage of flooding.
2. Water Flooding
After All Sand packs flooded by oil flooding, the second stage was water flooding. The experiment based on variable injected ratios according to basic pore volume of the sand pack (106.02875 cm^3). Appendix A.4. Then the economical cost have been checked for each flooding ratio to estimate the best economical value of injected ratio in secondary recovery.
3. Surfactant Solutions
Four solutions prepared for SDS surfactant according to Molecular weight (288.38) to specified the optimum conditions for surfactant flooding. The preparation based on water volume (1000 cm^3).
Then the surface tension has been calculated in the following conditions:
1. Surface Tension for SDS Solution in Different Concentrations

The surface tension of a liquid is an internal pressure caused by the attraction of molecules below the surface for those at the surface of a liquid. The surface tension (or interfacial tension if the interface is not a surface) determines the tendency for surfaces to establish contact with one another [22]. The Capillary Rise method have been used to determine the surface tension of SDS Solution. (Figure 7)
First: The densities of SDS solution in different concentrations were calculated and tabled. Then the Capillary Rise method used to investigate the surfactant solution ability to reduce the surface tension by using the following formula [23]:

$$\gamma = \frac{\rho \Delta h}{\frac{2}{g}\left(\frac{1}{r_1} - \frac{1}{r_2}\right)} \qquad \ldots(3)$$

Where:

γ = surface tension (dyne / cm)

ρ = density (gm / cm^3)

$\Delta h = h_1 - h_2$ which h_1 , h_2 the height of solution in capillary tubes in cm

g = gravity acceleration = 980 cm / sec^2

r_1 , r_2 = radius of capillary tubes in cm

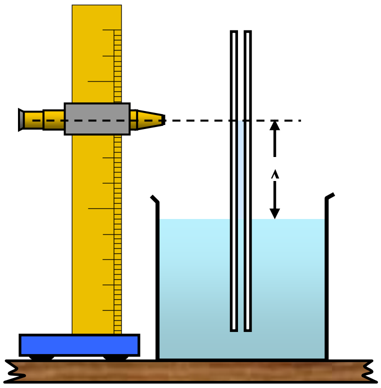

Fig. 7: Capillary Rise Method

0.063 and 0.3325 cm radius for capillary tubes were used in the experiment.

2. Calculation of Surface Tension for SDS Solution in Different Salinity Ratios

Four weights of NaCl were selected to prepare the solutions with SDS (10 $^{-2}$ molar) , water (salinity 500 P.P.M) and (500, 1000, 2500, 5000 P.P.M) of NaCl and in the same way the surface tension was calculated for each solution.

3. Calculation of Surface Tension for SDS Solution in Different Temperatures

The effect of temperature has been studied to select the optimum temperature for surfactants flooding. The solution selected which depended on the previous experiments (concentration, salinity) contains SDS solution in concentration equal to (10 $^{-2}$ molar) and 5500 P.P.M of total salinity and in the same way the surface tension has been calculated for the solution in different temperatures (40, 50 , 60 and 70 °C).

Surfactant Flooding

1. SDS Flooding (Anionic Surfactant)

First, five flooding processes have been done for SDS solution under pressure equal to 1000 psi and 2 cc/ sec for flow rate. These flooding processes represented injection ratios of 50%, 75%, 100%, 120% and 200% according to pore volume.

2. Criton X100 Flooding (Nonionic Surfactant)

Criton X100 solutions at the same conditions and under pressure equal to 1000 psi and 2 cc/ sec as flow rate injected for the same five PV% injected in SDS flooding. (Appendix A.8).

3. SDS Flooding Under Different Conditions at Constant Pore Volume

To study the effects of different conditions at fixed pore volume, twelve tests have been carried out, but at this tests sand packs with pore volume (37.2 cm^3) have been prepared. The pore volumes have been tabled in Appendix A.10. Also the remaining oil after secondary recovery has been measured (Appendix A.10). Three PV injected % considered according to the original pore volume which were 50, 120, 200 % respectively.

Four different conditions have been adopted for SDS surfactant as follow:

1- SDS concentration equal to 0.1 Molar , 3000 P.P.M for Salinity and 90 °C for temperature.

2- SDS concentration equal to 0.1 Molar, 1000 P.P.M for Salinity and 90 °C for temperature.

3- SDS concentration equal to 0.001 Molar, 3000 P.P.M for Salinity and 90 °C for temperature.

4- SDS concentration equal to 0.001 Molar, 1000 P.P.M for Salinity and 90 °C for temperature.

The pore volume was constant and the oil volume before SDS flooding was approximately constant (between 16.4 – 16.48 cm^3).

Results and Discussions

For each core holder the inside radius equal to 1.5 cm and height equal to 15 cm, so the volume of the core holder which also represent the bulk volume of sand pack for sand pack No.1 will be: Volume of all sand pack (bulk volume) = π r2 h = 3.1416 × 1.52 × 15 = 106.02875 cm^3.

The calculations of porosity for all sand packs have been tabled in Appendix A.1.

The calculation of porosity showed a range (33.86 % to 35.84%). According to Safarzadeh et al (2011) [24], the sand pack porosity was approximately 30% as shown in Figure 8.

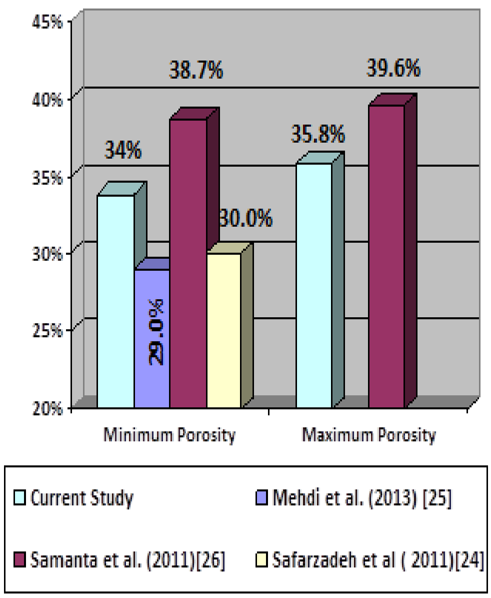

Fig. 8: comparison of porosity values in current study with previous studies

Permeability Measurement

Pressure drops at different flow rates were measured as in Table 3. Then qμ/A was plotted versus ΔP/L. A straight line which was crossed through the origin can be fitted to the data. The slope of the line represents the permeability of the sand pack. There may have been an experimental artifact in the data, If the data deviate significantly or systematically from the linear trend. Eight core holders were used in this stage of research, the value of 1500 Psi was neglected (Table 4), (Figure 9), Appendix A.2.

Table 3: values of Pressure and flow rates in oil flooding

Core Holder No.	ΔP (psi)	Q (cm^3/sec)
1	250	0.879
2	450	1.289
3	500	1.367
4	650	1.465
5	700	1.742
6	820	1.987
7	1000	2.259
8	1500	3.180

Table 4: values of permeability by Darcy Equation (2)

qμ /A	ΔP /L	K m.d (Calculated)
1.673917	1.133787	1476
2.454697	2.040816	1203
2.603236	2.267574	1148
2.789861	2.947846	946
3.317364	3.174603	1045
3.783928	3.718821	1017
4.301909	4.535147	948
6.055808	6.802721	890

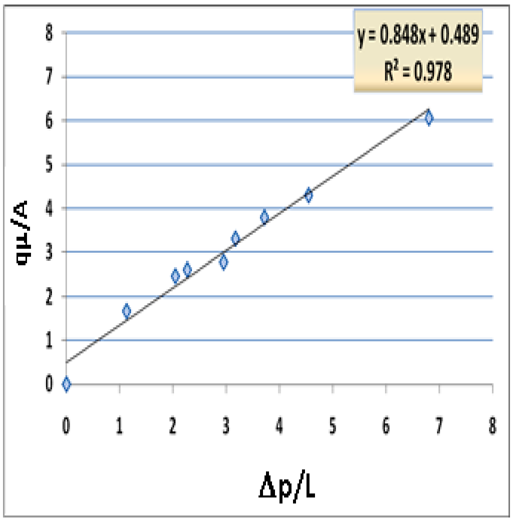

Fig. 9: Calculation of Permeability By using Darcy's Equation

K avg. = Slope = 848 m.d

The following relationships were used for conversion the units to Darcy's units.

$$cSt = \frac{cP}{SG} \text{ or } cP = cSt * SG \qquad \dots(4)$$

Where:
cSt = viscosity in cente stock
cP= viscosity in cente poise
SG= specific gravity
Pressure 1 pound per square inch = 0.068 atm.
The comparison between the permeability obtained from current study and previous studies shown in Figure 10.

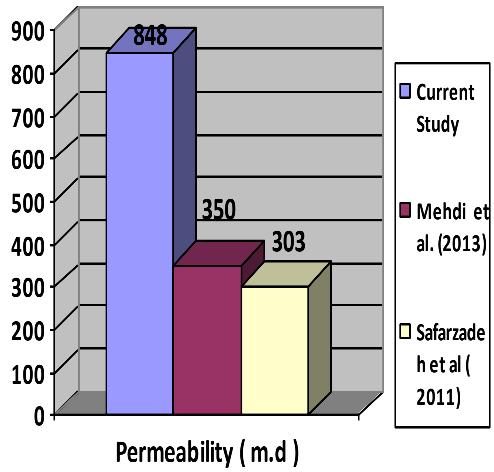

Fig. 10: Permeability (m.d) comparison between current study and previous studies

Water Flooding

Many injection ratios were experimented which represented 50%, 75%, 90%, 100%, 120%, 200%, 400%, 600% and 800% of the pore volume at flow rate 5 cc/sec for all PV ratios to check the best value of PV which match with economical limits, then the oil and water for each sand pack from secondary recovery process collected and separated, the oil volumes calculated, so the recovery percent became available to estimate as in appendix A.4 and Figure 11.

The water flooding results showed minimum recovery factor % was 39.892% at injection ratio 50% of pore volume and maximum value 66.7% at 800%.

The difference may be due to the difference in porosity and permeability of the sand packs that prepared and also to the difference in oil properties. Figure 12.

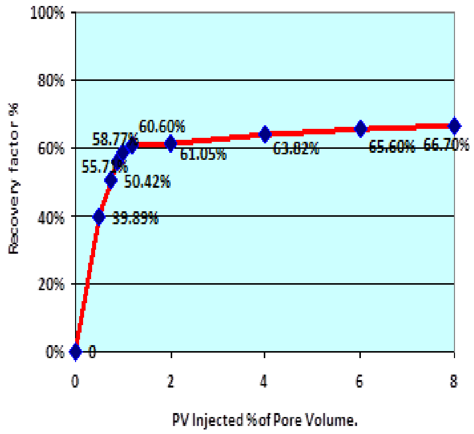

Fig. 11: Secondary Recovery factor % according to of PV injected % of Pore volume

According to results the P.V injected at 120% for the pore volume was the best volume due to slightly changes in oil recovery factor with highly costs when the P.V injected have been increased more than 120%.

A second oil and water flooding processes for seven core holders were done in the same procedure. (Appendixes A.6, A.7).

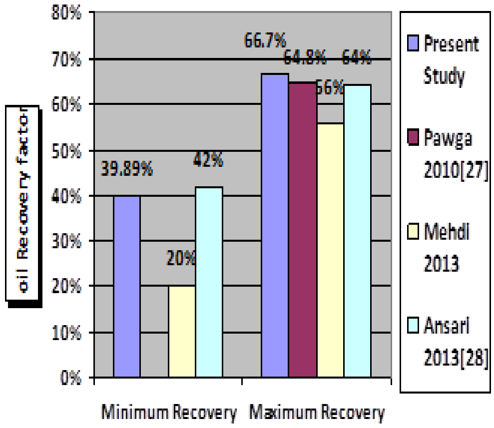

Fig. 12: Comparison for secondary recovery factor % between the present Study and Previous studies

Schaefer, 2012 [29], estimated the water injection's price for secondary recovery (5 - 10 $/bbl), so according to Table 5 and Figure 13 for water injection cost 5 $ / bbl, the PV injected for more than 100% for oil PV after primary recovery approximately double increased and that must be considered economically and will be useful in determination the start point of the tertiary recovery.

Table 5: % of increase in oil recovery factor according to % increase of PV Injected calculated to every 100 bbl of oil

PV Injected %	Recovery factor%	Additional cost $/ bbl oil
50%	39.892	6.267
75 %	50.415	7.438
90 %	55.714	8.077
100 %	58.77	8.508
120%	60.2%	9.967
200 %	61.05	16.38
400%	63.82	31.34
600%	65.5	45.8
800%	66.7	59.97

According to results the P.V injected at 100% for the pore volume was the best volume due to economical limits.

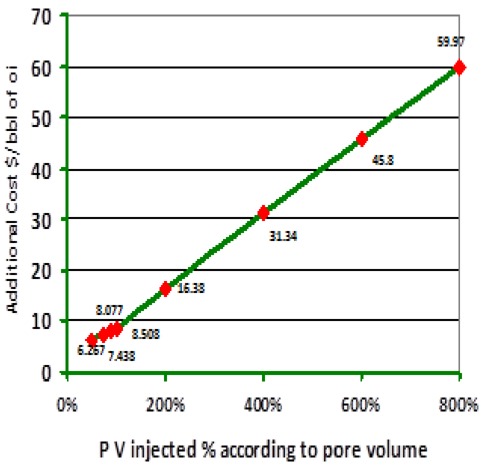

Fig. 13: additional cost in $/bbl according to PV injected

Surfactant Solutions

Table 6 show the preparation of four SDS solutions in different concentrations and it's densities in room temperature 30 °C listed in Table 7.

Table 6: preparation of four SDS solutions

SDS Weight gm	Resulting Solution Molar
28.838	10^{-1}
2.8838	10^{-2}
0.28838	10^{-3}
0.028838	10^{-4}

Table 7: Density of SDS solutions

Concentration of SDS Solution (Molar)	Density (gm / cm^3)
10^{-1}	0.9903
10^{-2}	0.9822
10^{-3}	0.9702
10^{-4}	0.9552

Calculation Of Surface Tension

1. For SDS Solution at Different Concentrations

The results obtained from Capillary Rise method for four different SDS concentrations showed that the best concentration was 0.01 Molar as in Table 8.

Table 8: surface tension values by Capillary Rise method

SDS Conc. In Molar	Density gm / cm^3	h_1 cm	h_2 cm	Δh Cm	γ dyne/cm
10^{-1}	0.9903	2.179	1.55	0.629	23.724
10^{-2}	0.9822	4.80	4.289	0.611	22.856
10^{-3}	0.9702	4.513	3.8853	0.6277	23.194
10^{-4}	0.9552	5.232	4.59	0.642	23.356

The concentration of 10^{-2} molar selected to check the effect of salinity. Figure 14.

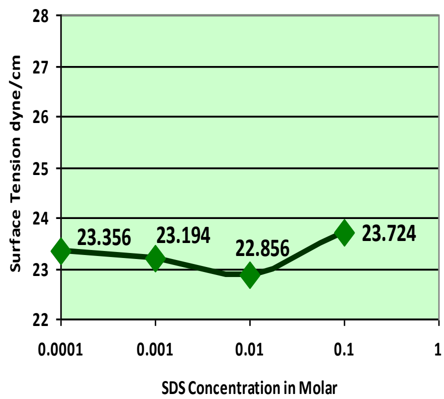

Fig. 14: effect of SDS concentration on surface tension values

Wang et al. 2013 experimented the surface tension of either fresh and produced water with three types of polymer surfactant and they found a range of surface tension of fresh water between 22.15 and 23.14 dyne /cm as for a concentration of polymer between 200 -1000 mg/ L [30].
Raney et al. 2011 found the optimum ASP concentration to obtained the lower interfacial tension was 10^{-3} molar [31].

2. Calculations of Surface Tension for SDS Solution in Different Salinity Values

The effect of salinity has been represented by different NaCl Values in P.P.M have been experimented to select the best salinity according to lower surface tension values (Table 9).

Table 9: surface tension values for SDS Solution + NaCl

Water Salinity P.P.M	NaCl P.P.M	Density gm/cm^3	Δh Cm	γ dyne/cm	γ Variation dyne/cm according to reference value 22.856
500	500	0.9820	0.705	26.368	+ 3.512
	1000	0.9817	0.665	24.864	+ 2.008
	2500	0.9811	0.59	22.0462	- 0.8098
	5000	0.9805	0.52	19.4187	- 3.4373

The result showed that the SDS surfactant with water in concentration (0.01 molar) and with addition of 5000 P.P.M for NaCl (5500 P.P.M salinity in total) gave the lower surface tension in comparison with the other conditions that have been experimented. Figure 15.

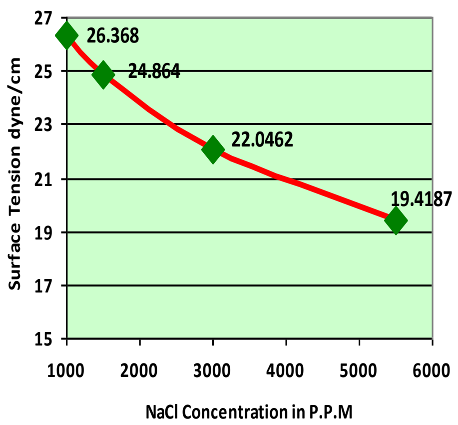

Fig. 15: effect of NaCl concentration on surface tension values

Liu, (2008) [32] resulted that the optimum salinity for ASP flooding was 4000 P.P.M. while Mwangi, (2010) indicated that the best salinity for surfactant flooding was 4000 P.P.M.

Nasralla et al. (2011) [33] took a best results of oil recovery by using water with a salinity 5000 P.P.M, while Samanta et al. (2011) [26] results showed a surface tension range for SDS surfactant with addition of PHPA polymer and NaCl between 32 dyne / cm at 0 P.P.M and 34 dyne/ cm at 2000 P.P.M. The comparison of salinity values between current study and previous studies showed a significant convergence of salinity used as the best condition for surfactant solution as shown in Figure 16.

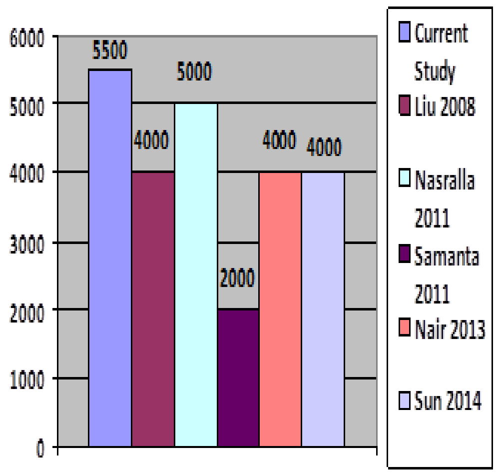

Fig. 16: A comparison of the Optimum Salinity between current study and previous studies

3. Calculation of Surface Tension for SDS Solution in Different Temperatures

The effect of temperature has been studied by examining different temperatures for SDS solution in concentration equal to 0.01 molar and 5500 P.P.M for salinity. The result as shown in Table 10.

The result showed that the SDS surfactant with water in concentration (0.01 molar) and with addition of 5500 P.P.M for salinity in 70 °C represented best result in order to the less surface tension in comparison with the other temperatures that have been experimented. As shown in Figure 17.

Table 10: surface tension values for SDS solution in different temperatures

Temp. °C	h_1 cm	h_2 cm	Δh Cm	γ dyne/cm	γ Variation dyne/cm according to value 19.4187
30	2.02	1.50	0.52	19.4187	0
40	1.995	1.51	0.485	18.1117	- 1.307
50	1.863	1.386	0.477	17.813	- 1.6057
60	1.821	1.363	0.468	17.477	- 1.942
70	1.804	1.355	0.459	17.141	- 2.2777

Thornton, (1974) [34] indicated that for SDS solution (0.1 Molar) and 5000 P.P.M, the best temperature for minimum surface tension was 80 °C. No specific change in surface tension value when temperature was varied from 80 °C to 70 °C.

Tang et al. (2006) [35] found the optimum temperature for SDS solution at 90 °C. For SDS solution between 0.005 to 0.01 molar at 70 °C the surface tension differences could not been noticed.

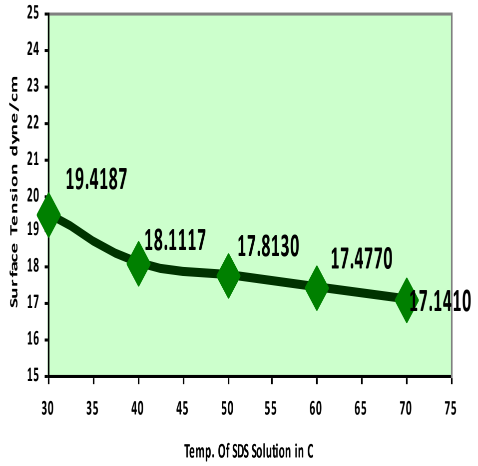

Fig. 17: surface tension values in different temperatures for SDS Solution

Safarzadeh et al (2011) [17] and Mehdi et al. (2013) [15] used sand pack model for surfactant flooding at 70 °C. The results as shown in Figure 18 indicated a clear convergence in temperatures used in best condition of SDS solution between current study and previous studies.

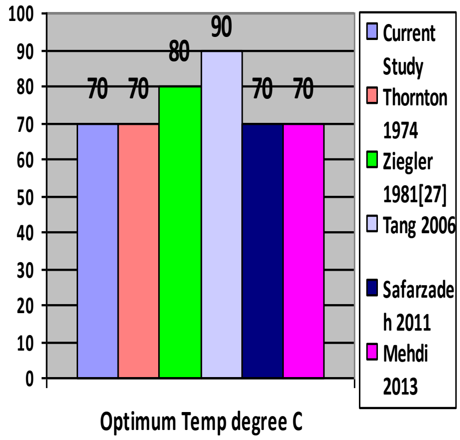

Fig. 18: A comparison of the Optimum Temperatures For Different Studies

Surfactant Flooding

The properties of solution selected for surfactant flooding listed in Table 11.

Table 11: Surfactant Solution's Properties

Property (Unit)	Sand pack
Concentration (mol/L)	0.01
Salinity (P.P.M)	5500
Test Temp.	70°C

1. SDS Flooding (Anionic Surfactant)

Flooding processes represented injection ratios of 50%, 75% , 100%, 120% and 200% according to pore volume indicated that 67.58% of oil volume has been recovered after SDS flooding according to oil volume remained in the PV with injection ratio 120% and 89.4% could be recovered after both secondary and tertiary flooding at the same injection ratio. The results have been tabled in Appendix A.5 and represented in Figure 19.

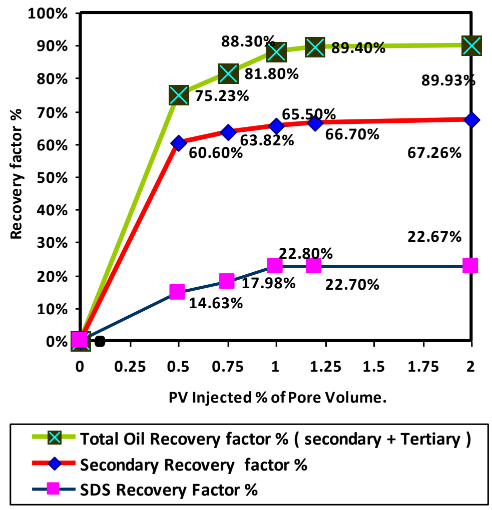

Fig. 19: SDS Recovery factor % for % of PV injected

According to Safarzadeh et al (2014) [37], the RF% was 87% for SDS flooding at the same circumstances. Figure 20.

According to Figure 19 the best SDS recovery economically and quantitatively was 120% PV injected.

The result also indicated to semi match for recovery factor % result obtained at PV injected rates (50% - 100%) between water flooding and SDS flooding.

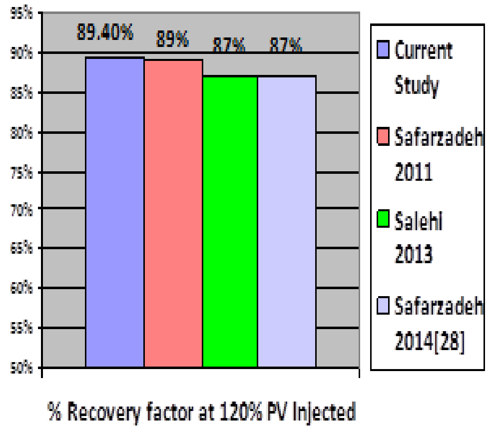

Fig. 20: % Oil Recovery factor comparison for different researches

2. Criton X100 Flooding (Nonionic Surfactant)

The results of criton X100 flooding showed that at 120% PV, the RF% was 84.14 % by both secondary and tertiary recovery, while 85.6% recovered at 200% PV (Figure 21).

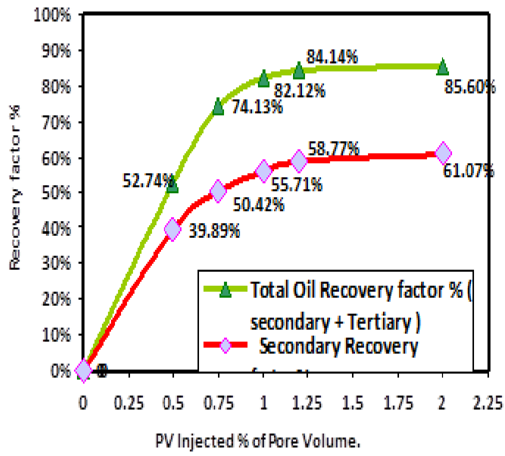

Fig. 21: Criton X100 recovery factor % for % of PV injected

3. CTAB Flooding (Cationic Surfactant)

The results clarified that about 85% of oil has been recovered at 120% PV by both secondary and tertiary recovery, while 86% recovered at 200% PV. The result shown in Figure 22.

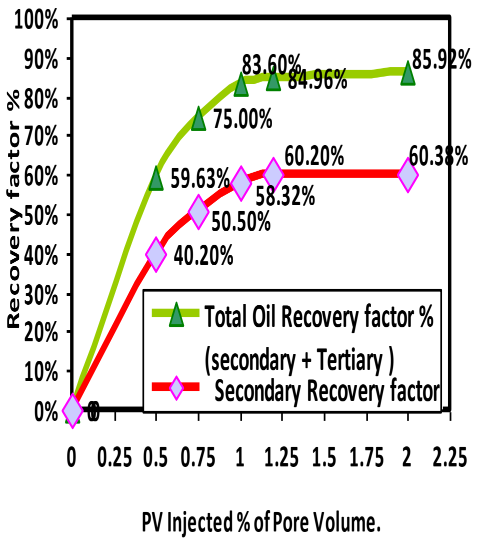

Fig. 22: CTAB Recovery factor % for % of PV injected

Comparison Between Surfactants According to RF %

The results obtained in this study distinct in clearly image that the anionic surfactant SDS was the best surfactant according to productivity as in Figure 23. The results as represented in Figure 16 demonstrated that oil recovery factor % in Criton X100 and CTAB flooding were very closely at PV injected ≥ 75%.

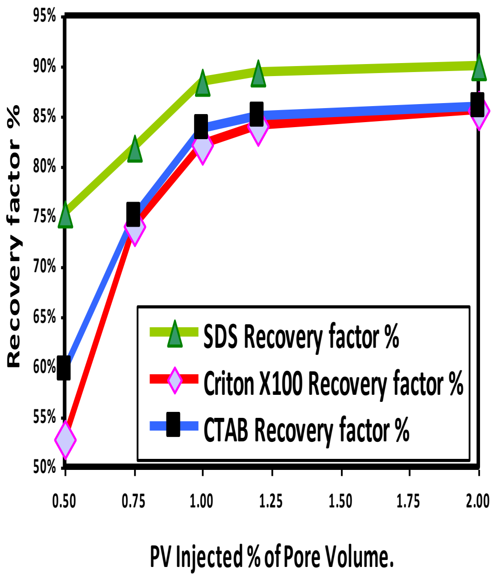

Fig. 23: comparison of RF % according to the surfactant type

Comparison Between Surfactants Economically

Based on the International price , the prices of SDS , Criton X100 and CTAB in recent time is 1000-1300 US $/ Metric Tons, 63 US $/Lit and 1000-5000 US $/ Metric Tons respectively. According to mathematical relations:

- The total cost of one barrel of SDS is about 0.6$.
- For Criton X100, 100.1$ /bbl
- For CTAB, 2.9$ /bbl.

And according to the difficulty of handling for Criton X100 because the liquid form , expensive cost and low recovery in comparison with SDS and also because of the approximate similarity between Criton X100 and CTAB, it's prefer to use SDS in surfactant flooding.

SDS Flooding Under Different Conditions at Constant Pore Volume

The results of 15 flooding processes matched the result of the study when the surface tension values have been taken in consideration to determine the optimum conditions for SDS flooding to ensure maximum oil recovery. Figure 24.

Comparison Between RF % Obtained Under Different Conditions at Constant Oil PV and 90 °C

The results shows in clearly image that the best conditions for surfactant flooding as adopted before depending on the surface tension indicator. The overall comparison between all conditions of experiments plotted in Figure 25.

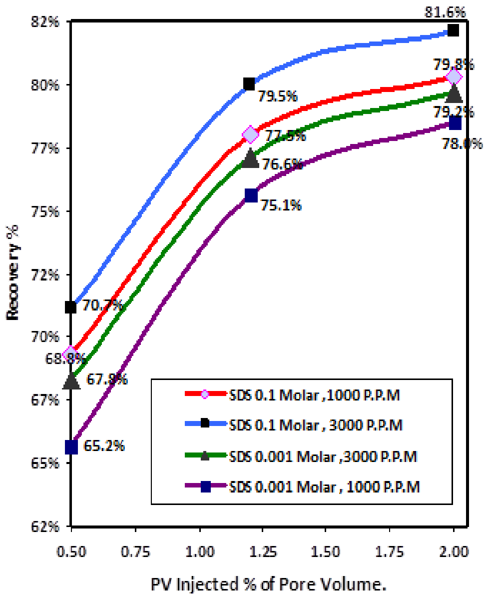

Fig. 24: RF % of SDS at different conditions

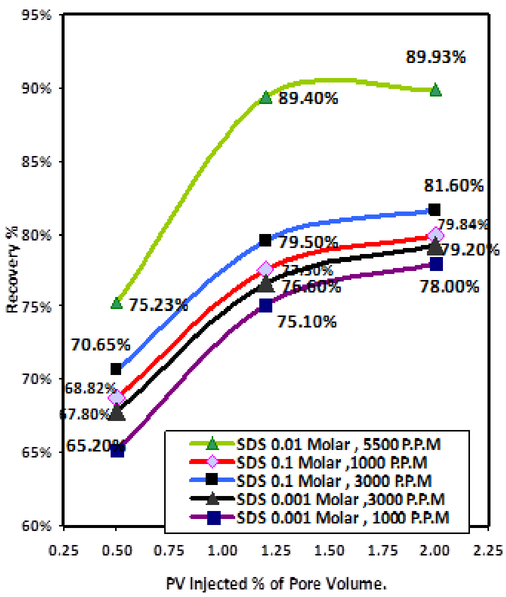

Fig. 25: comparison of oil recovery factor % with different conditions (Concentration, Salinity) at constant Pore Volume and 90 °C

Conclusions

The following conclusions are obtained from this study:

1. The permeability values which calculated by mathematical method (Darcy equation) showed a clear differences comparing with graphical method due to many reasons such as differences in grain size , packing and reduction in flow rate in spite of high pressure according to the blockage of the sieve , so best fit line has been taken as experimental artifact of permeability.
2. Secondary recovery by water flooding did not showing any significant effects when the injection ratio exceeded 1.2 PV because the recovery factor % increase slightly (60.2% at 1.2 PV – 66.7% at 8.0 PV).
3. The result of this study indicated that the best PV rate for water injection was 1.2 PV. Productively, while the optimum injection rate was 1.0 PV economically.
4. It is clearly that the cost of water injection in secondary recovery increased 700% when PV injected increased from 1.0 PV to 8.0 PV, while the recovery increased only 8% (58.77 – 66.7%).
5. Use of 0.01% molar of SDS and 500 P.P.M salinity reduced density about 2% and use additional 5000 P.P.M of NaCl reduced surface tension value about 15%. Furthermore, increasing temperature from 30 – 70 °C will resulting additional surface tension reduction about 12%, so as a result of all additions, surface tension reduced about 25%. So, the tests of surface tension led to identify the optimum conditions for tertiary recovery by using surfactant flooding . These conditions included 0.01 molar for concentration, 5500 P.P.M for salinity and 70 °C for temperature.
6. All surfactant formulations were successful in terms of producing significant amounts of additional incremental oil (after water flooding), but the best oil recovery factor % obtained from SDS flooding was better than the same operation at the same conditions by either Criton X100 or CTAB which were 89.94%, 85.6% and 85.9% respectively.

7. Again the 1.2 PV rate for surfactants injection was the best value economically because it was obviously that recovery factor % by SDS, Criton X100 and CTAB increased 0.54%, 1.46% and 0.96% respectively when the PV rate changed from 1.2 PV to 2.0 PV.
8. According to the results and surfactant prices , the best surfactant Productively and economically was SDS then CTAB while Criton X100 was very expensive and inadequate unless additives have been used to improve the specifications of solution and reduce the cost to minimum value.

References

1. S. Q. Tunio, A. H. Tunio, N. A. Ghirano, and Z. M. El Adawy, "Comparison of different enhanced oil recovery techniques for better oil productivity," *International Journal of Applied Science and Technology*,vol. 1, 2011.
2. T. I. First, "Waterflooding method," United States 3126952 A Patent, 1964.
3. G. P. Ahearn and W. W. Gale, "Surfactant-waterflooding process," ed: US Patent 3,302,713, 1967.
4. L. Holm, "Miscibility and miscible displacement," *Journal of Petroleum Technology*, vol. 38, pp. 817-818, 1986.
5. M. Cissokho, S. Boussour, P. Cordier, H. Bertin, and G. Hamon, "Low salinity oil recovery on clayey sandstone: Experimental study," *Petrophysics*, vol. 51, p. 305, 2010.
6. S. Buelow Sandersen, "Enhanced oil recovery with surfactant flooding," Ph.D. Thesis, Technical University of Denmark 2012.
7. S. Shaddel and Tabatabae-Nejad, "Low Salinity Water flooding and Combination of Low Salinity Water flooding with Surfactant and Alkaline Injection to Improve Oil Recovery - Core Flooding Experiments," pp. Paper 3-121, 2013.
8. G. Hirasaki, C. A. Miller, and M. Puerto, "Recent advances in surfactant EOR," *SPE Journal,* vol. 16, pp. 889-907, 2011.
9. S. Iglauer, Y. Wu, P. Shuler, Y. Tang, and W. A. Goddard III, "New surfactant classes for enhanced oil recovery and their tertiary oil recovery potential," *Journal of Petroleum science and Engineering,* vol. 71, pp. 23-29, 2010.
10. C. I. S. Pwaga, O. Hundseth, F. J. Parales, M. U. Idress, "Comparative Study of Different EOR Methods," Department of Petroleum Engineering, Norwegian University of Science & Technology, Trondheim, Norway, 2010.
11. M. A. Gholamzadeh and M. Chahardahcherik, "Optimization of Injection rate and Injection Time for Surfactant and Water Floodings in Oil Fields," *International Journal of Advancements in Research & Technology*, vol. 1, pp. 1-7, 2012.
12. L. Xu, "Optimizing Surfactant Additives for Low-Permeability Wet Gas Formations: A Laboratory Approach for Correlating Capillary Pressure and Emulsion Tendency with Surfactant Performance," presented at the SPE Eastern Regional Meeting, Pittsburgh, Pennsylvania, USA, 2013.
13. K. Ma, "Transport of surfactant and foam in porous media for enhanced oil recovery processes," Ph.D Degree, RICE UNIVERSITY, Houston, USA 2013.
14. A. Habibi, S. Ayatollahi, S. Ashoorian, and M. Masihi, "Effect of Time and Temperature on Crude Oil Aging to do a Right Surfactant Flooding with a New Approach," in *OTC-24801-MS, Offshore*

Technology Conference-Asia, Kuala Lumpur, Malaysia, 2014.

15. S. Iglauer, M. Sarmadivaleh, C. Geng, and M. Lebedev, "In-situ Residual Oil Saturation And Cluster Size Distribution In Sandstones After Surfactant and Polymer Flooding Imaged With X-ray Micro-computed Tomography," in *IPTC 17312: International Petroleum Technology Conference*, Doha, Qatar, 2014.
16. T. Nguyen, W. Bae, and T. Dang, "Improvements of Mixed-surfactants in Alkaline/Surfactant/Polymer Solutions," Petroleum Science and Technology, vol. 32, pp. 1458-1464, 2014.
17. L. Sun, K. Spildo, K. Djurhuus, and A. Skauge, "Salinity Selection for a Low Salinity Water-Low Salinity Surfactant Process," Journal of Dispersion Science and Technology, vol. 35, pp. 551-555, 2014.
18. H. H. Hussain, "Laboratory Study of Improving The Transportation Efficiency Of Oil In Pipes," M.Sc Thesis, Petroleum Engineering Department University Of Baghdad, Baghdad, 2007.
19. A. chemika. (2014). SDS http://www. Alphachemika-scientific.com/chemicals.htm.
20. C. Book. (2014). Sodium dodecyl sulfate,http://www.chemicalbook.com/ChemicalProductProperty_EN_CB2147453.htm.
21. C. F. Chemical, "http://www. cdhfinechemical.com/products/ laboratory-chemicals.asp .", 2014.
22. S. Tripathi, "Importance of surfactant adsorption in soil & ground water remediation," Bachelor of Technology, Chemical Engineering, National Institute of Technology Rourkela, Orissa, India, 2007.
23. T. Dang-Vu and J. Hupka, "Characterization of porous materials by capillary rise method," Physicochemical problems of mineral processing, vol. 39, pp. 47-65, 2005.
24. S. A. T. N. a. E. S. Mohammad Amin Safarzadeh, "Experimental Investigation of the Effect of Calcium Lignosulfonate on Adsorption Phenomenon in Surfactant Alternative Gas Injection," Journal of Chemical and Petroleum Engineering, University of Tehran, vol. 45, pp. 141-151, 2011.
25. M. S. Mehdi, S. Eghbal, and A. T. N. Seyyed, "Experimental study of new improved oil recovery from heavy and semi-heavy oil reservoirs by implementing immiscible heated surfactant alternating gas injection," Journal of Petroleum and Gas Engineering, vol. 4, pp. 154-159, 2013.
26. A. Samanta, K. Ojha, A. Sarkar, and A. Mandal, "Surfactant and Surfactant-Polymer Flooding for Enhanced Oil Recovery," Advances in Petroleum Exploration and Development, vol. 2, pp. 13-18, 2011.
27. C. I. S. Pwaga, O. Hundseth, F. J. Parales, M. U. Idress, "Comparative Study of Different EOR Methods," Department of Petroleum Engineering, Norwegian University of Science & Technology, Trondheim, Norway, 2010.
28. A. Ansari, M. Haroun, N. Al Kindy, B. Ali, R. A. Shrestha, H. Sarma, and A. Dhabi, "Electrokinetics Assisted Surfactant-EOR to Optimize Mature Waterfloods in AbuDhabi Carbonate Reservoirs," presented at the SPE Asia Pacific Oil & Gas Conference and Exhibition, 2013 Jakarta, Indonesia, 2013.

29. K. SCHAEFER. (2012). Waterfloods: The Next Big Profit Phase of the Shale Oil Revolution, http://oilandgas-investments.com/2012 /energy-services/waterfloods-the-next-big-profit-phase-of-the-shale-revolution/.
30. K.-L. Wang, L.-L. Zhang, X. Li, and Y.-Y. Ming, "Experimental Study on the Properties and Displacement Effects of Polymer Surfactant Solution," Journal of Chemistry, vol. 2013, 2013.
31. S. Kirk Raney, S. S. Ayirala, S. R. Chin, and S. P. Verbeek, "Surface and Subsurface Requirements for Successful Implementation of Offshore Chemical Enhanced Oil Recovery," 2011.
32. S. Liu, "Alkaline Surfactant Polymer Enhanced Oil Recovery Process," PhD Thesis, Chemical Engineering, RICE UNIVERSITY, HOUSTON, TEXAS, 2008.
33. R. A. Nasralla, M. B. Alotaibi, and H. A. Nasr-El-Din, "Efficiency of oil Recovery by low salinity water flooding in sandstone reservoirs," in SPE Western North American Region Meeting, 2011.
34. J. A. Thornton, "Influence of apparatus geometry and deposition conditions on the structure and topography of thick sputtered coatings," Journal of Vacuum Science & Technology, vol. 11, pp. 666-670, 1974.
35. Y. Tang, B. Du, J. Yang, and Y. Zhang, "Temperature effects on surface activity and application in oxidation of toluene derivatives of CTAB-SDS with KMnO4," Journal of Chemical Sciences, vol. 118, pp. 281-285, 2006.
36. V. M. Ziegler and L. L. Handy, "Effect of temperature on surfactant adsorption in porous media," Society of Petroleum Engineers Journal, vol. 21, pp. 218-228, 1981.
37. S. A. T. N. Mohammad Amin Safarzadeh, Eghbal Sahraei, and and M. M. Salehi, "An Experimental Examination of Adsorption Phenomenon in Foamassisted Water Alternative Gas: The Effect of Injection Rate," Iranian Journal of Oil & Gas Science and Technology, http://ijogst.put.ac.ir, vol. 3 (2014), pp. pp. 37-50, 2014.

Appendix A.1

Sample No.	Weight (Pipe + Sand) gm	Weight (Pipe + Sand + Water) gm	Water Weight (gm)	φ %
1	1064.4	1101.7	37.3	35.18
2	1064.7	1101.5	36.8	34.71
3	1057.9	1093.8	35.9	33.859
4	1077.7	1114.3	36.6	34.519
5	1078.4	1114.7	36.3	34.236
6	1057.6	1094.8	37.2	35.085
7	1058.6	1096.6	38.0	35.84
8	1061.6	1098.0	36.4	34.33

Appendix A.2

Sample No.	Δp Psi	Δp atm.	Q cm^3/sec	ΔP /L	qμ/A
1	250	17.0115	4.445	1.1341	3.50563
2	450	30.62	5.987	2.04133	4.797916
3	500	34.023	6.752	2.2682	5.025845
4	650	44.23	9.241	2.94867	5.590733
5	700	47.6322	9.68	3.17548	7.281764
6	820	55.798	10.768	3.72	10.31752
7	1000	68.046	14.025	4.5364	3.108443
8	1500	102.069	19.872	6.8046	2.307839

Appendix A.3

Sample No.	Weight (Pipe + Sand) gm	Weight (Pipe + Sand + Oil) gm	Oil Weight (gm)	ρ_{oil} gm/cm^3	V_{oil} cm^3
1	1064.4	1090.4	26.0	0.879	29.58
2	1064.7	1091.2	26.5		30.15
3	1057.9	1090.6	32.7		37.2
4	1077.7	1112.4	34.7		39.476
5	1078.4	1107.2	28.8		32.7645
6	1057.6	1087.9	30.3		34.471
7	1058.6	1089.6	31.0		35.2674
8	1061.6	1094.6	34.0		38.68

Appendix A.4

Sample No.	PV injected % according to PV_{core}	V_{oil} cm^3	V_{oil} Secondary Recovery Cm^3	Recovery %
1	50	29.58	11.8	39.892
2	75	30.15	15.2	50.415
3	90	37.2	20.8	55.714
4	100	39.476	23.2	58.77
14	120	35.722	21.5	60.2
5	200	32.7645	19.85	60.6
6	400	34.471	22	63.82
7	600	35.2674	23.1	65.5
8	800	38.68	25.8	66.7

Appendix A.5

Sample No.	PV % injected to PV_{core}	V_{oil} cm^3	V_{oil} Secondary Recovery Cm^3	V_{oil} after Sec. Recovery Cm^3	V_{oil} Tertiary Recovery (SDS) Cm^3	Recovery % to Sec. Recovery	Recovery % to total V_{oil}
5	50	32.7645	19.85	12.9145	4.8	37.17	75.23
6	75	34.471	22	12.471	6.2	49.71	81.8
7	100	35.2674	23.1	12.1674	7.45	61.23	88.3
8	200	38.68	25.8	12.88	8.95	69.49	89.94
4	120	39.1	26.3	12.8	8.65	67.58	89.4

Appendix A.6

Sample No.	Weight (Pipe + Sand) Gm	Weight (Pipe + Sand + Oil) gm	Oil Weight (gm)	ρ_{oil} gm/cm^3	V_{oil} cm^3
9	1063.7	1097.3	34.35	0.879	39.1
10	1062.6	1093.4	30.8		35.04
11	1061.7	1094.5	32.8		37.315
12	1059.8	1093.4	33.6		38.225
13	1060.3	1090.9	30.6		34.81
14	1065.2	1096.6	31.4		35.722
15	1066.1	1095.0	28.9		32.88

Appendix A.7

Sample No.	**PV injected % according to PV_{core}**	**V_{oil} cm^3**	**V_{oil} Secondary Recovery Cm^3**	**Recovery %**
9	100	39.1	23.2	59.33
10	200	35.04	21.4	61.07
11	50	37.315	15	40.2
12	75	38.225	19.3	50.5
13	100	34.81	20.3	58.32
14	120	35.722	21.5	60.2
15	200	32.88	20	60.83

Appendix A.8

Sample No.	**PV % injected to PV_{core}**	**V_{oil} cm^3**	**V_{oil} Secondary Recovery Cm^3**	**V_{oil} After Secondary Recove0ry Cm^3**	**V_{oil} Tertiary Recovery Cm^3 (Criton)**	**Recovery % to Sec. Recovery**	**Recovery % to total V_{oil}**
1	50	29.58	11.8	17.78	3.8	21.37	52.74
2	75	30.15	15.2	14.95	7.15	43.48	74.13
3	100	37.2	20.8	16.4	9.75	59.45	82.12
9	120	39.1	23.2	15.9	9.7	61.00	84.14
10	200	35.04	21.4	13.64	8.6	63.05	85.6

Appendix A.9

Sample No.	**PV injected % according to PV_{core}**	**V_{oil} cm^3**	**V_{oil} Secondary Recovery Cm^3**	**V_{oil} After Secondary Recovery Cm^3**	**V_{oil} Tertiary Recovery Cm^3 (CTAB)**	**Recovery % to Sec. Recovery**	**Recovery % to total V_{oil}**
11	50	37.315	15	22.315	7.25	32.49	59.63
12	75	38.225	19.3	18.95	9.37	45.38	75%
13	100	34.81	20.3	14.51	8.8	60.65	83.6
14	120	35.722	21.5	14.222	8.85	62.23	84.96
15	200	32.88	20	12.88	8.25	64.05	85.92

Appendix A.10

Sample No.	**PV % injected to PV_{core}**	**Conditions**	**V_{oil} after Sec. Recovery Cm^3**	**SDS Injected Volume Cm^3**	**V_{oil} Tertiary Recovery (SDS) Cm^3**	**Recovery % to total V_{oil}**
1	50	0.1 Molar (SDS) 1000 P.P.M salinity 90 °C	16.4	18.6	9.2	68.82
2	120		16.42	44.46	12.4	77.5
3	200		16.4	74.4	13.3	79.84
4	50	0.1 Molar (SDS) 3000 P.P.M salinity 90 °C	16.48	18.6	9.8	70.65
5	120		16.46	44.46	13.1	79.5
6	200		16.45	74.4	13.9	81.6
7	50	0.001 Molar (SDS) 1000 P.P.M salinity 90 °C	16.44	18.6	7.8	65.2
8	120		16.43	44.46	11.5	75.1
9	200		16.42	74.4	12.6	78.0
10	50	0.001 Molar (SDS) 3000 P.P.M salinity 90 °C	16.4	18.6	8.82	67.8
11	120		16.4	44.46	12.1	76.6
12	200		16.42	74.4	13.0	79.2