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Surfactant-induced flow behavior effects in gas condensate reservoirs

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**SURFACTANT-INDUCED FLOW BEHAVIOR EFFECTS IN GAS CONDENSATE
RESERVOIRS**

A Thesis

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Master of Science in Petroleum Engineering

in

The Department of Petroleum Engineering

By

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B.E. (Chem.), NIT Karnataka, India, 2000
December, 2010

DEDICATION

This work is dedicated to all my teachers, my family and my friends...

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I take this opportunity to extend my heartfelt thanks to my advisor Dr. Dandina Rao for accepting me to be his student and for his able guidance, continued encouragement and for the much needed funds for the project. I also extend my thanks to Dr. Stephen Sears and Dr. Mileva Radonjic for their kind acceptance to serve as members on the examination committee.

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TABLE OF CONTENTS

DEDICATION	ii
ACKNOWLEDGEMENTS	iii
LIST OF TABLES	vi
LIST OF FIGURES	vii
NOMENCLATURE	ix
ABSTRACT	x
CHAPTER 1: INTRODUCTION	1
1.1 Background	1
1.2 Objective	5
1.3 Methodology	7
CHAPTER 2: LITERATURE REVIEW	8
2.1 Deliverability Reduction in Gas Condensate Reservoirs	8
2.2 Relative Permeability Studies	10
2.3 Treatment of Condensate Blockage	16
2.4 Phase Behavior Studies	18
2.5 Surfactants	23
CHAPTER 3: EXPERIMENTAL APPARATUS AND PROCEDURE	30
3.1 Experimental Apparatus	30
3.2 Experimental Procedure	32
3.2.1 Core Preparation	32
3.2.2 Saturation of the Core	33
3.2.3 Establishing Irreducible Water Saturation (S_{wi})	33
3.2.4 Artificial Retrograde Gas Condensate Mixture Preparation	33
3.2.5 Core Flood Procedure of Gas Mixture	38
3.2.6 Subsequent Retrograde Gas Floods	39
CHAPTER 4: RESULTS AND DISCUSSION	40
4.1 Saturation with Brine without Surfactant (i.e. 0 ppm Surfactant Concentration)	41
4.2 Saturation with Brine Containing 1000 ppm Surfactant Concentration	44
4.3 Saturation with Brine Containing 2000 ppm Surfactant Concentration	46
4.4 Saturation with Brine Containing 5000 ppm Surfactant Concentration	47
4.5 Comparative Analysis of Pressure Drops	49
4.6 Economic Impact Evaluation	53

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS.....	56
5.1 Summary and Conclusions.....	56
5.2 Recommendations for Future Work.....	57
REFERENCES	58
VITA.....	63

LIST OF TABLES

Table 3.1 Artificial condensate compositions.....	34
Table 3.2 Artificial condensate composition	36
Table 4.1 Different cases considered in experimentation.....	40
Table 4.2 Core properties for a typical core	41
Table 4.3 Summary of important results.....	52
Table 4.4 Typical gas composition for the well.....	53
Table 4.5 Typical Parameters for the well	54
Table 4.6 Gas flow rate for various cases.....	54

LIST OF FIGURES

FIGURE 1.1 PROJECTION OF GLOBAL NATURAL GAS DEMAND UPTO 2035.....	1
FIGURE 1.2 PHASE ENVELOPE OF TYPICAL GAS CONDENSATE MIXTURE	3
FIGURE 1.3 FLOW REGIONS FOR A RADIAL WELL PRODUCING FROM A GAS COND. RESERVOIR	4
FIGURE 1.4 SCHEMATIC DEPICTION OF THE SPREADING COEFFICIENT	6
FIGURE 1.5 OIL-WATER-GAS DISTRIBUTIONS IN O/G/W/R SYSTEMS	6
FIGURE 3.1 SCHEMATIC OF THE EXPERIMENTAL APPARATUS	30
FIGURE 3.2 PICTURE OF THE EXPERIMENTAL APPARATUS	32
FIGURE 3.3 PT PHASE DIAGRAM FOR THE COMPOSITION 85%C1, 5%NC4, 10%NC7-MIXTURE 1 ..	35
FIGURE 3.4 PT PHASE DIAGRAM FOR THE COMPOSITION 85%C1, 4%NC4, 11%NC7-MIXTURE 2 ..	35
FIGURE 3.5 PT PHASE DIAGRAM FOR THE COMPOSITION 85%C1, 3%NC4, 12%NC7-MIXTURE 3 ..	36
FIGURE 3.6 PT PHASE DIAGRAM FOR THE RETROGRADE GAS.....	37
FIGURE 3.7 LIQUID DROP OUT CURVE CALCULATED USING PR EOS AT 73 ⁰ F.....	37
FIGURE 4.1 PRESSURE DROP ABOVE AND BELOW DEW POINT FOR BRINE WITHOUT SURFACTANT ...	42
FIGURE 4.2 RELATIVE PERMEABILITY ABOVE DEW POINT PRESSURE.....	43
FIGURE 4.3 RELATIVE PERMEABILITY BELOW DEW POINT – BRINE WITHOUT SURFACTANT.....	43
FIGURE 4.4 PRESSURE DROP COMPARISON BETWEEN 1000 PPM & BRINE WITHOUT SURFACTANT ..	44
FIGURE 4.5 RELATIVE PERMEABILITY BELOW DEW POINT – 1000 PPM SURFACTANT CASE	45
FIGURE 4.6 RELATIVE PERMEABILITY BELOW DEW POINT – 2000 PPM SURFACTANT CASE	45
FIGURE 4.7 PRESSURE DROP COMPARISON BETWEEN 2000 PPM & BRINE WITHOUT SURFACTANT ..	46
FIGURE 4.8 PRESSURE DROP COMPARISON BETWEEN 5000 PPM & BRINE WITHOUT SURFACTANT ..	47
FIGURE 4.9 RELATIVE PERMEABILITY BELOW DEW POINT – 5000 PPM SURFACTANT CASE	48
FIGURE 4.10 PRESSURE DROP COMPARISON BETWEEN 5000 PPM AND 2000 PPM SURFACTANT	48
FIGURE 4.11 PRESSURE DROP COMPARISON FOR ALL FOUR CASES	49
FIGURE 4.12 EFFECT OF SURFACTANT CONCENTRATION ON ΔP AT VARIOUS FLOW RATES.....	50

FIGURE 4.13 EFFECT OF SURFACTANT CONCENTRATION ON DIMENSIONLESS ΔP (DLPD) 51

FIGURE 4.14 INCREMENTAL REVENUE PER YEAR VS WELL BOTTOM HOLE PRESSURE..... 55

NOMENCLATURE

r_w	= Radius of wellbore
S_{wi}	= Irreducible water saturation
S_o	= Spreading coefficient
O	= Oil
W	= Water
G	= Gas
R	= Rock
M	= Electropositive element
X	= Halide
k_{rg}	= Gas relative permeability
k_{ro}	= Oil relative permeability
k_{rc}	= Condensate relative permeability
N_c	= Capillary Number
σ_{og}	= Free energy of oil-gas interface or oil-gas interfacial tension
σ_{ow}	= Free energy of oil-water interface or oil-water interfacial tension
σ_{wg}	= Free energy of water-gas interface or water-gas interfacial tension

ABSTRACT

Natural gas, which accounts for a quarter of world's energy, has been a major energy source because of its abundance and less impact on environment. With explorations at higher depth, pressure and temperature, the share of gas condensate reservoirs to global gas production is increasing. A unique production challenge associated with these reservoirs is the condensate blockage problem, which is the buildup of condensate liquid saturation around wellbore as a result of drawdown below dew point pressure. Mitigation of this problem requires in depth understanding of the multiphase flow of liquid and gas. Surfactants are well known in the literature for affecting such multiphase flow characteristics in reservoirs. They affect the flow behavior primarily by wettability alteration as well as spreading coefficient modification. In this study, multiphase flow characteristics of gas condensates, with and without surfactants were observed by running corefloods representing actual reservoir retrograde condensation phenomena. A commercial anionic surfactant, Alfoterra® 123-4S, was successfully shown to facilitate condensate removal with relative permeability enhancement of over 17 percent at a surfactant concentration of 2000 ppm, which was also the optimum concentration under the flowing conditions. The efficacy of surfactant was observed to be a non-linear function of its concentration and this is attributed mainly to the pleateauing effect above the critical micellar concentration (CMC) values.

CHAPTER 1: INTRODUCTION

1.1 Background

Natural gas is fast becoming a key energy source and its demand has been rising steadily in the last few decades. At present, natural gas provides around a quarter of the total energy and is rapidly catching up with oil as a primary energy source.

From 1973 to 2007, the contribution of oil to the world's energy supply dropped from 46.1 % to 34.0 %, with the increasing use of natural gas accounting for that decline. Total natural gas consumption is projected to increase by 44% from 108 trillion cubic feet (tcf) in 2007 to 156 trillion cubic feet (tcf) in 2035 as per International Energy Outlook (IEO) 2010 report published by US Energy Information Administration (US EIA). Figure 1.1 shows the projection of natural gas consumption till 2035.

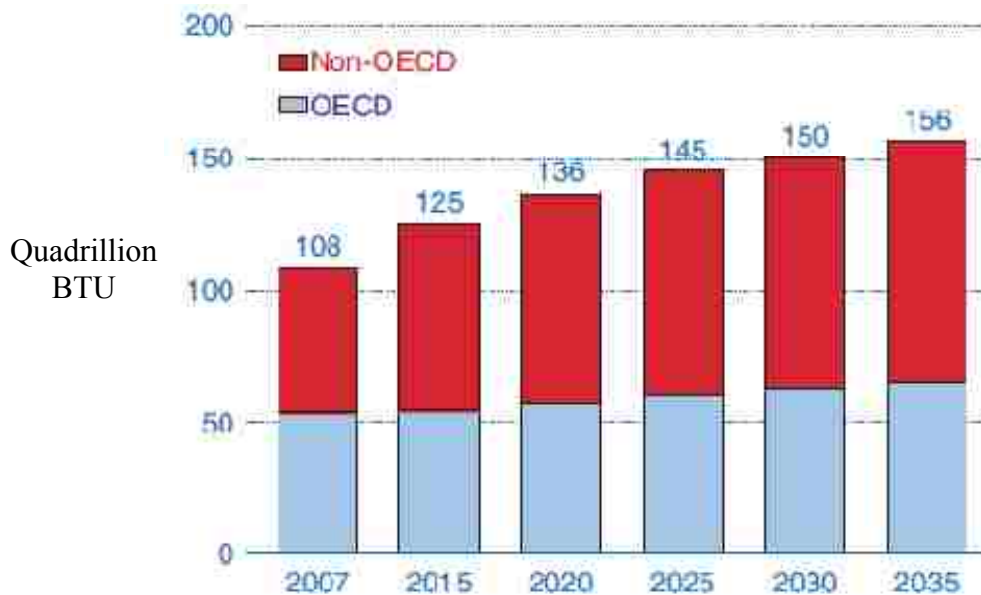


Figure 1.1 Projection of global natural gas demand upto 2035

(Courtesy: U.S. Energy Information Administration/International Energy Outlook 2010)

The popularity of natural gas as an energy source is because of its abundant reserves, less impact on environment (as it's the cleanest amongst fossil fuels due to complete burning) and multiple

applications across different sectors. This increased usage of natural gas worldwide is leading to more long term sales contracts between producers and consumers for various critical applications and that require accurate forecasting of production performance from these reservoirs. However, unlike dry gas reservoir engineering computations for gas condensate systems present some unique challenges and most prominent is the condensate blockage or condensate banking problem. This phenomenon called condensate banking is the buildup of condensate liquid saturation around wellbore as a result of drawdown below the dew point pressure. As a result of this build up, gas flow to the wellbore gets severely restricted eventually leading to the well getting ceased. Afidick et al. (1994) and Barnum et al. (1995) have reported field cases in which productivity declined by a factor of two to four as result of condensate blockage. Unfortunately, some of the world's huge gas fields are gas condensate reservoirs like Arun gas field in Indonesia, Shtokmanovskoye in Russia, Karachaganak field in Kazakhstan and Cupiagua field in Columbia. The importance of gas condensate fields is on the rise due to increased share of gas produced from these fields amongst global gas production. Gas condensate fields are more frequently encountered as explorations are taking place at higher depths and higher temperatures and pressures. Thus understanding the physics of gas condensate buildup, its remediation and the multiphase flow of gas and liquid is increasingly becoming all the more important.

A typical gas condensate reservoir might exist as a single phase gas at the point of discovery when the reservoir pressure is above the dew point pressure. As the production continues from the reservoir, the pressure declines isothermally. When the bottom hole flowing pressure of the well goes below the dew point pressure, condensation starts occurring. The term retrograde condensation has been used to describe this anomalous behavior of condensation from gas phase with isothermal decrease in pressure. Figure 1.2 illustrates this process of retrograde condensation along the isothermal reservoir depletion line. At point A in the figure, the

retrograde gas mixture exists as a single phase gas. On isothermal depletion along the depletion line shown A-B, the two phase region is encountered below the dew point line. The quality or isovol lines, depicted by hashed lines in the figure, give the volume by volume ratio of liquid in the mixture as it undergoes retrograde condensation. As the pressure depletes, more and more condensates form and liquid volume increases, however, on further decrease of pressure, revaporization occurs. This can be seen from the isovol lines intersecting the depletion line twice inside the phase envelope. Though this revaporization would supposedly counter the condensate blockage but this would occur very late in the life of a reservoir.

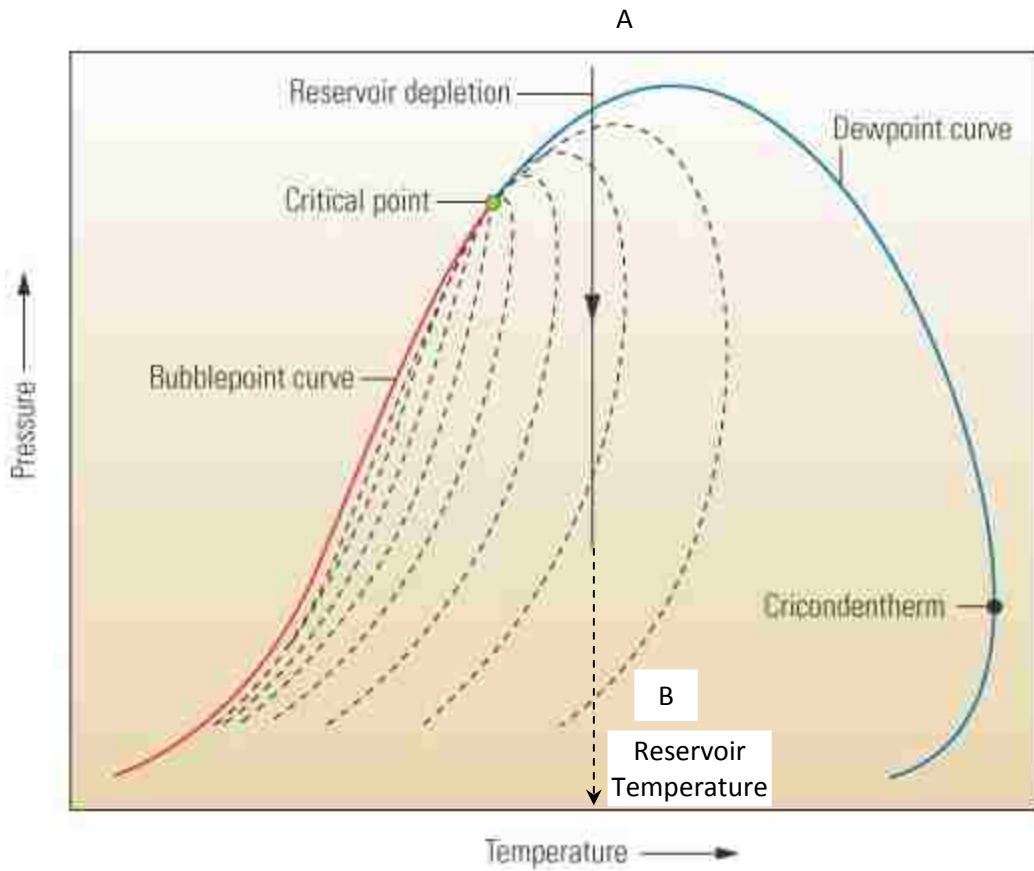


Figure 1.2 Phase envelope of typical gas condensate mixture
 (Courtesy: <http://www.glossary.oilfield.slb.com>)

This condensate accumulation starts around the wellbore and gradually propagates radially into the reservoir. Fevang et al. (Figure 1.3) showed that three regions (in a typical process) are

created around the wellbore. A near well region I where both gas and condensate flow, an intermediate region II where condensate builds up but is unable to flow as it is below the critical saturation, outer region III that contains only single phase gas.

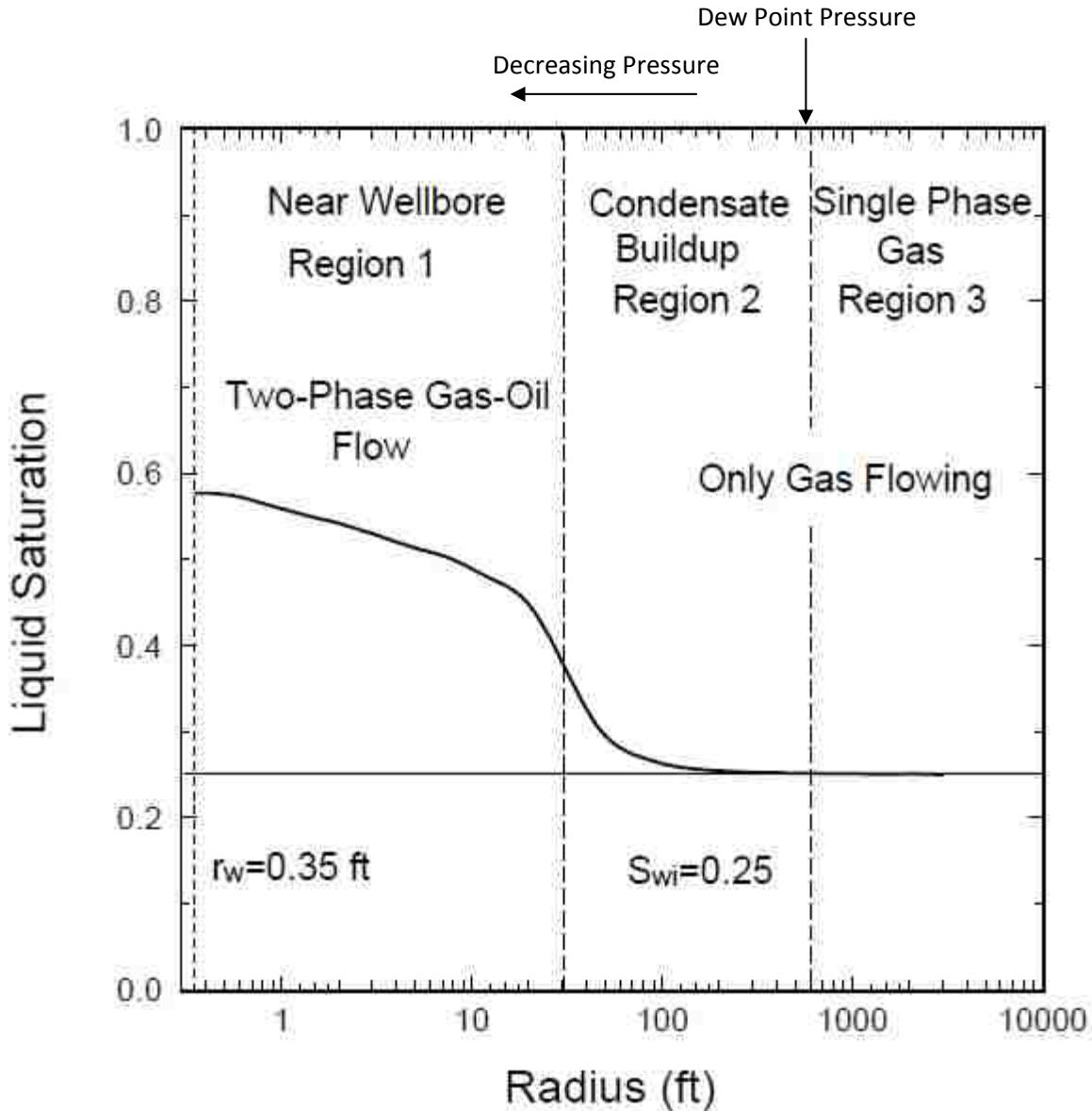


Figure 1.3 Flow regions for a radial well producing from a gas cond. reservoir
(Courtesy: Fevang et al. -1995)

As the reservoir pressure falls below the dew point pressure, the region II extends well into the reservoir. Region I also extends by extending into region II. Thus the curve shifts to the right with time. This condensate banking around wellbore results in restricted flow of gas into the well

bore and thus gas productivity declines. For a given producing condition, one or two regions may exist.

Various methods have been proposed in the literature for remediation of this condensate banking problem. Prominent among them are managing the drawdown pressure to keep the well bottom hole pressure above the dew point pressure, methanol injection, gas recycling, hydraulic fracturing etc. These methods have been applied with limited success as their results are temporary²⁴.

Altering the wettability of the region to intermediate wet by use of surfactants is seen as a permanent solution to this problem. It is believed that such wettability alteration will reduce the liquid saturation near the wellbore but field tests with reservoir fluids have been scarce to quantify such effects. Some have also worked on the spreading coefficient modification in relation to critical condensate saturation but as in the case of wettability alteration, the quantification of the effect of such treatments with reservoir fluids has been sparse.

1.2 Objective

The spreading coefficient is used to describe fluid-fluid interactions. It signifies the imbalance of the fluid interfacial/surface tensions at water-oil, oil-gas and water-gas interfaces. The spreading coefficient can be either positive or negative. For the water-oil-gas system, the oil spreading coefficient S_o can be defined as below:

$$S_o = \sigma_{wg} - \sigma_{ow} - \sigma_{og} \text{ -----Equation 1}$$

Where, σ_{wg} is the water-gas interfacial tension, σ_{ow} is the water-oil interfacial tension, and σ_{og} is the oil-gas interfacial tension. The defining equation of the oil spreading coefficient is also displayed in Figure 1.4.

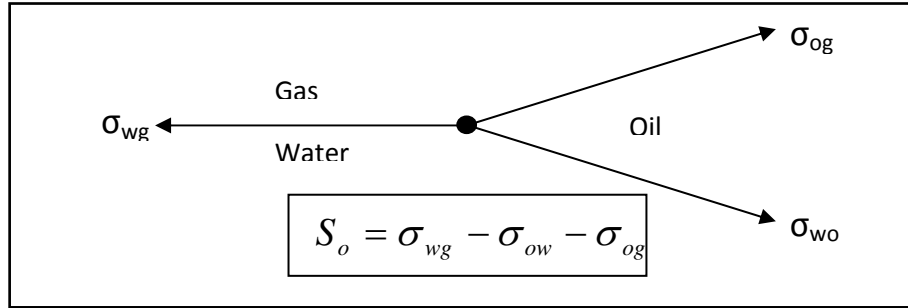


Figure 1.4 Schematic depiction of the spreading coefficient
(Courtesy: Rao et al. -2007)

If the spreading coefficient is positive ($S_o > 0$), it denotes that one of the tensions is larger than the sum of the other two and results in the total spreading of that fluid over the others, forming a continuous fluid layer; if it is negative ($S_o \leq 0$), non-spreading occurs and will lead to fluid lenses with a definite contact angle against the other two fluids.

Wettability states of reservoir rocks, water-wet or oil-wet, also lead to difference in spreading behavior. Figure 1.6 illustrates the distribution of water, oil and gas in the reservoir rock for two wettability states.

Wettability	Positive S_o	Negative S_o
Water Wet		
Oil Wet		

Figure 1.5 Oil-Water-Gas distributions in O/G/W/R systems
(Courtesy: Rao et al. -2007)

In case of water-wet rock surface, $S_o > 0$ leads to oil spreading between gas and water while $S_o < 0$ leads to oil lenses floating on the gas-water interface. On the other hand, if it is oil-wet, $S_o > 0$ leads to oil isolating gas and water by spreading between them and $S_o < 0$ leads to the flow of gas

and water phases as discrete globules entrained in the oil phase. In case of intermediate wet behavior, thin continuous oil film is likely to form along the entire length of flow channel facilitating its flow.

The objective in this study is to understand the flow behavior effects caused by surfactants in relation to retrograde condensate reservoirs that exhibit condensate blockage problems. The flow behavior effects are characterized by conducting core flood experiments with and without surfactants. In situ retrograde condensation is effected in the core flood experiments by designing and building in-house the core flood apparatus.

1.3 Methodology

Core flood experiments were conducted with and without surfactants to quantify the effect of surfactants in the flow behavior of gas condensates. This involved designing an experimental setup to create the in situ retrograde phenomenon that takes place in gas condensate reservoirs producing at bottom hole conditions below dew point pressure. A retrograde gas mixture composition that would undergo the condensation process in the experimental conditions was also generated using CMG-WinProp. Surfactants were administered during the saturation phase of the core and its effect was observed on the flow behavior of gas condensates. Series of experiments with increasing concentration of surfactants was carried out.

CHAPTER 2: LITERATURE REVIEW

This project is on surfactant induced flow behavior effects in case of gas condensate reservoirs. The literature on this area have been thoroughly investigated and reported in following categories.

2.1 Deliverability Reduction in Gas Condensate Reservoirs

Gas condensate reservoirs are a special class of their own as they produce both gas and condensate in sizable quantities. Gas condensate reservoirs contain only single phase gas at the point of discovery when the initial reservoir pressure is above the dew point pressure of the gas. However, as the production continues the reservoir pressure declines and goes below the dew point pressure. This results in condensation of the heavier components from the gas stream and is termed as retrograde condensation. For this retrograde condensation to happen, the temperature of the gas has to be between the critical temperature and the cricondenthem. This well known retrograde condensation leads to severe deliverability loss in a gas condensate well. The phenomenon of retrograde condensation is seen when the flowing bottom hole pressure of the well falls below the dew point pressure with the reservoir pressure still above it. This causes the buildup of liquid condensate ring around the wellbore and leads to severe loss in gas phase relative permeability. This phenomenon has been known in the industry as “condensate banking” and is known to decrease the well productivity severely. A glaring example of condensate banking effects is in Arun field in Indonesia. Here a maximum liquid dropout of 1.1% by volume led to productivity decline as high as 50%, as reported by Afidick et al. (1994)

➤ **Flow regions:** As discussed by Fevang and Whitson (1996), gas condensate flow and saturation distribution in gas condensate reservoirs can be conceptually classified into three regions (as shown in Figure 1.4):

- Region 1: A near-well region where both gas and oil flow.

- Region 2: A two phase condensate buildup region where only gas is flowing.
- Region 3: A region containing only single phase gas.

For a given producing condition, one, two or all three regions may exist. These three regions define pseudosteady state flow conditions, meaning that they represent steady state conditions at a given time but that these steady state conditions change gradually during depletion.

- **Region 1:** A near-well region where the gas and oil flow is in steady state. This region has pressure below the dew point pressure and the condensate saturation is high, at or above the critical saturation, which makes both gas as well as condensate phases mobile. The flowing composition within region 1 is constant throughout.
- **Region 2:** This is the intermediate region where the pressure is slightly below dew point pressure and the condensate buildup starts. Saturation remains very low but increases in time, however, the condensate saturation is below the critical saturation and hence condensate flow does not occur. Here the gas flows at reduced flow rate.
- **Region 3:** Beyond region (2) there is an outer region where pressures are above the initial dew point pressure and no condensate saturation is found here. This region has single phase gas only which forms the sole mobile phase.

Danesh et al. (1988) carried out micro model and core studies of the flow of gas condensates and the phenomena of retrograde condensation. Through micro model studies they observed that the initial formation of condensate in reservoir pores below dew point is a film wise process maintaining hydraulic continuity throughout the pores. The occurrence of condensate film flow and the low value of interfacial tension below dew point in retrograde condensation region lower the significance of capillarity relative to gravitational and viscous effects. He also observed that the minimum condensate saturation for the downward flow of condensate may be quite low especially in high permeability rocks.

Cvetkovic et al. (1990) carried out rich gas condensates reservoirs (specific gravity >0.75) production studies. Their conclusion from simulation studies was that gas condensate can significantly affect the relative permeability to gas. However one of their claim that condensate problem is not significant for lean gas is not commensurate with the productivity loss field example from Arun field in Indonesia, which has maximum liquid dropout of only 1.1% while experiencing a 50% drop in gas productivity with an average reservoir pressure of 7100 psia and temperature of 352⁰F, reported by Afidick et al. (1994).

Barnum et al. (1995) has presented a case history of a well producing retrograde gas that ceased production below dew point pressure. Two case studies have also been presented which exhibit productivity index reduction due to condensation ranging from 20% to 50%. The field data analyzed suggested gas recoveries below 50% are limited to reservoirs below 1000 mD-ft.

Novosad (1996) carried out simulation studies and found that a near well liquid bank, far in excess of that given by fluid retrograde curve, forms within hours of bottom hole flowing pressure falling below the saturation pressure. This is the case for lean as well as rich fluids regardless of reservoir permeability.

2.2 Relative Permeability Studies

Relative permeability is a measure of the relative conductivity of a phase through a porous medium in the presence of other fluids and or phases. It is defined as the ratio of the effective permeability to the absolute permeability of the porous media. Relative permeability is a very important parameter in understanding relative ease of fluid flow through the porous media when multiple phases are competing to flow simultaneously.

There are two broad ways, viz., steady state and unsteady state methods¹⁹, in which the relative permeability of a porous medium to fluid phases can be determined. The steady state method for a two phase fluid system basically involves injecting two phases at a certain volumetric ratio

until stabilization of both the pressure drop across the core and the effluent volumetric ratios. The saturations of the two fluids in the core are then determined, typically, by weighing the core or by performing mass balance calculation for each phase. Individual relative permeability data are calculated from the direct application of Darcy's law. Even though the calculation of relative permeabilities is rather simple, the entire process can be time consuming, as the time required for achieving a steady state may be inordinate. Additionally, if mass balance is used for the determination of saturations, the procedure involves repeated removing and mounting of the core samples after every step that can lead to fluid loss and damage to the core during the disassembly and reassembly process causing errors in the measure saturations and resulting relative permeabilities.

The unsteady state method is primarily based on the interpretation of an immiscible displacement process. For a two-phase system: basically a core that is either in the preserved state or restored state after cleaning and aging, at the saturation conditions that exist in the reservoir, is flooded with one of the displacing phases. Typically, the flood phase is gas (for gas-oil relative permeability) or water (for oil-water relative permeability) since in the reservoir one or the other of these phases displaces the oil. For the determination of relative permeability data from the unsteady method, two different methods can be used for the calculation of water saturation: the *alternate* method and the *Johnson-Bossler-Neumann* method also known as the *JBN* method. *Buckley and Leverett* developed in 1955 the equations governing the displacement of one fluid by another in a porous medium. They assumed linear, incompressible flow and negligible capillary forces. Ten years later, *Welge* presented a method based on Buckley Leverett theory to calculate the saturations and the ratio of relative permeabilities of the displacing phase and displaced phase.

Asar et al. (1988) conducted coreflood experiments using methane-propane mixtures to understand the effect of interfacial tension on gas-oil relative permeabilities. The experiments were conducted near the saturation pressures to get interfacial tensions over a range. They concluded that the relative permeability curves approach straight line curves when the fluids approach miscible conditions, marked by IFT values approaching zero. They observed steeper decrease in oil relative permeability compared to gas relative permeability as the IFT values increased. They also noted that the approach of miscibility conditions led to lower residual saturations for oil and gas phases.

Munkerud (1989) showed that relative permeability curves to the gas condensate model system in a depletion process are similar to curves of ordinary gas oil systems, and that gravitational segregation of condensate is pronounced even at liquid saturation below the critical saturation for flow. He concluded through dynamic displacement experiments of retrograde liquid that the relative permeability to gas showed strong dependence on interfacial tension between the two phases.

Haniff et al.(1990) conducted experiments with two component methane-propane gas condensate system and has found that there exists a critical value of interfacial tension (0.05 mN m^{-1}) below which capillary forces are negligible and the fluid distribution is such that the liquid spreads along the pore walls and gas occupies the centre of the pores. He says in conditions of negligible capillary forces “free surface” of liquid is transported across “surface of seepage thereby maintaining hydraulic continuity and this is what leads to high recovery of liquid.

Fevang et al. (1996) has identified three regions of flow in gas condensate wells with BHFP lower than the dew point pressure, namely, Region I with constant flowing composition (GOR) where both gas and liquid flow simultaneously and this region causes the most of the deliverability losses, Region II with condensate accumulation but no condensate flow, Region III

with gas as single phase only. He states that the primary relative permeability relationship affecting well deliverability is k_{rg} as a function of k_{rg}/k_{ro} and that saturations do not enter the calculations.

Blom et al. (1997) measured a series of two phase relative permeabilities at the near-critical conditions by means of displacement method using methanol/n-hexane system. They have concluded that relative permeability curves at near critical conditions are strongly dependant on interfacial tension and flow rate. They observed a clear trend from immiscible to miscible relative permeability curves with decreasing interfacial tension and increasing flow rate.

Henderson et al. (1998) has conducted steady state relative permeability tests using gas condensate fluids and have shown that the relative permeability was rate sensitive. The relative permeabilities of both phases increased as the velocity increased. They observed that at higher IFT values gas and condensate relative permeabilities were reduced; however the rate effect was still evident especially for the gas phase and this effect was independent of core effects. They have attributed the relative permeability rate effect to the process of condensation in conjunction with the flow characteristics of gas condensate fluids, which leads to the redistribution of fluids as flow rate increases, with a minimum change in saturation.

Sumnu-Dindoruk et al. (1998) have taken field automation data such as production rate and recoveries available from field to estimate gas relative permeability as an alternative to laboratory measured relative permeability data. The relative permeabilities they calculated were well within the input curves. The data used by them for the relative permeability estimation were gas and condensate surface production rates, gas in place (GIP), initial pressure (P_i), Connate water saturation (S_{wc}) and PVT properties.

Whitson et al. (1999) conducted relative permeability measurements and based on steady state measurements of several gas condensate systems concluded that the key relation defining steady

state flow in gas condensate wells is k_{rg} as a function of k_{rg}/k_{ro} . They have found that the effect of hysteresis is minimal in the fundamental permeability relation $k_{rg} = f(k_{rg}/k_{ro})$. They have found that the effect of capillary number on gas oil relative permeability can result in a significant improvement in gas relative permeability and thus minimizing the negative impact of condensate blockage.

Mott et al. (1999) used pseudo steady technique for the first time to measure gas condensate relative permeabilities k_{rg} as a function of k_{rg}/k_{ro} and capillary number. They too reported a significant increase in relative permeability with velocity. They used depletion technique to measure gas relative permeability at low flow rates and found that at those rates there was no rate dependency but they evidenced increased relative permeability with lower IFT.

Chen et al. (1999) carried out core flood experiments on gas condensate flow behavior for two North Sea gas condensate reservoirs with the objective of measuring the effects of rock and fluid characteristics on critical condensate saturation as well as gas relative permeability. They used recombined North Sea gas condensate reservoir fluids from separator oil and synthetic gas for their experiments. The cores used were composite cores of approximately 29" length made from 2- 3" long core plugs. Their results showed that critical condensate saturation and relative permeability are sensitive to both flow rate and interfacial tension. Their condensate relative permeability (k_{rc}) results exhibited an unusual convex curvature when plotted against condensate saturation. They attributed this unusual behavior of reduction in condensate relative permeability (k_{rc}) with increasing condensate saturation to a strong inverse relationship between k_{rc} and IFT.

Al-Anazi et al. (2002) conducted steady state two phase core flood experiments in Berea sandstone and Texas Cream limestone to quantify the loss in relative permeability caused by condensate accumulation. They have shown that such relative permeability losses can occur in high permeability reservoirs as well, contrary to the popular notion that condensate blocking

around wells in high permeability reservoirs is not significant. Gas relative permeability reductions of 91% to 95% were seen in 2-5 mD limestone cores and 95% to 98% in 246-378 mD sandstone cores. They also observed a more severe reduction in gas relative permeability during two phase flow for higher water saturations than at lower water saturations at a pressure of 1200 psia and temperature of 145⁰F.

Al-Honi et al. (2004) conducted core flood experiments on gas condensate flow behavior for a Libyan gas condensate behavior. The results of the test on the reduction in gas permeability due to retrograde condensate accumulation demonstrated that, in general, the effective permeability to gas decreased significantly at pressure below the dew point pressure due to condensate trapping effect in all the core stacks (composite) that were investigated. They noticed that permeability continued to drop at very low pressures even though theoretically condensate was to revaporize. The recoveries of the liquid condensate during the vaporization by dry gas injection at pressures below the dew point pressure were very high. The recovery ranged from 66% to 70% for the high permeability core stack and 86% to 98% for the lower permeability core stack. They found this recovery to be less than 100% though in theory it is possible to get all condensate revaporized into the methane gas stream. This discrepancy was attributed to macroscopic sweep efficiency and mass transfer limitations within the rock matrix.

Ayyalasomayajula et al. (2005) used pseudo steady laboratory core flood experiments with synthetic fluids coupled with fine scale compositional simulation and showed that condensate banking is the cause of 60% to 80% loss in well productivity observed in the field. Their laboratory measured relative permeability showed increasing trend with increase in capillary number and with increasing values of the k_{rg}/k_{ro} ratio. However, their data did not show any trend with the rock quality. They were able to fit their data with the currently available relative permeability models but were not able to fit the entire range of their data.

Bang et al. (2006) made measurements of gas and oil relative permeabilities at high capillary numbers corresponding to the near well region of high rate gas condensate wells. Gas and oil relative permeabilities showed strong dependence on capillary numbers at high capillary number for both sandstones and limestones. They used UT relative permeability to fit their data and found that the model was able to fit their data over a wide range of capillary numbers, k_{rg}/k_{ro} ratio, rock type, fluids, temperatures, permeability and initial water saturation using just one set of parameters for all the data.

App et al. (2009) measured gas condensate relative permeability for a rich gas/condensate reservoir using a live, single phase reservoir fluid. They performed two phase flow tests across a range of pressures and flow rates to simulate reservoir conditions from initial production through depletion. They also performed a single phase multi-rate experiment to assess inertial or non Darcy effect. They observed a dramatic increase in both gas and condensate relative permeabilities with increasing capillary number. They also observed that the measured condensate relative permeabilities were greater than gas relative permeabilities for rich gas/condensate fluids at high capillary (N_c) numbers. The measured gas relative permeabilities were low compared with most gas/condensate systems, which they attributed to the richness of the fluid samples.

2.3 Treatment of Condensate Blockage

Du et al. (2000) Conducted experiments with gas condensate to evaluate the efficacy of methanol in restoring gas relative permeability upon retrograde condensation. The methanol was found to increase the gas relative permeability by a factor of 1.2 to 2.5 depending on the initial water saturation. They have cited miscible displacement of condensate and water by methanol for this improvement. They further stated that condensate buildup may not occur as long methanol is in the pore spaces or even when buildup occurs, the effective permeability would still be higher

because of absence of water in the pore spaces. Beneficial effects of methanol are more pronounced at higher water saturations.

Al-Anazi et al. (2003) conducted field test for methanol treatment on Hatter's pond field in Alabama, which showed retrograde condensation behavior. They reported gas and condensate productivity increase by a factor of 2 for the first four months and 50% thereafter. The increases in gas and condensate production rates were sustained over at least 4 month period.

Liu et al. (2006) used a relatively cheap chemical WA12, which was also stable at a temperature of 170° C and salinity of 70000 ppm to alter the wettability of a low permeability rock from water wittedness to gas wittedness. They observed increase in gas phase relative permeabilities at residual water saturation by about two times as well as the recoveries and productivities. The reported decrease of residual water saturation by gas flooding was from 42.38% to 26.77%.

Garzon et al. (2006) carried out laboratory coreflood tests with carbonate cores as well as field trial with inhibited diesel to evaluate its effectiveness in removing condensate banking. They obtained improved results in gas relative permeabilities with inhibited diesel in both cases. At 60% MS concentration (vol. /vol.) with diesel they obtained maximum improvement in gas productivity.

Fahes et al. (2007) carried out experimental investigation to test the effectiveness and durability of treatment at high temperatures using various treatment chemicals and the effect of wettability alteration on liquid mobility and gas productivity. They were successfully able to alter the wettability from liquid wetting to intermediate gas wetting as demonstrated by contact angle and imbibition tests using chemicals. They observed increased liquid mobility as well as gas productivity due to wettability alteration. The absorption of new chemicals onto the rock surface did not decrease the absolute permeability of rock.

Liu et al. (2008) carried out pilot study to demonstrate the improvement in gas productivity as a result of wettability alteration based on experimental studies. They applied a fluorocarbon surfactant, meant to alter the wettability to gas wetness, to a gas condensate field in Dongpu field and found significant increase in gas productivity though the increase in gas production did not sustain long, which they attributed to low permeability and high viscosity of the liquid condensate.

Bang et al. (2008) carried out core flood experiments using both outcrop sandstone and reservoir rocks to measure the effect of liquid blocking on gas relative permeability as well as developed a chemical treatment to reduce the damage caused by blocking by altering the wettability of water wet sandstone to neutral wet. They used a non-ionic polymeric fluorinated surfactant delivered in 2-butoxyethanol/ethanol and PG/IPA mixtures. They confirmed the wettability alteration after the chemical treatment by measuring the USBM wettability index of the treated reservoir cores and notice significant surfactant adsorption of rock surface. They observed improvement in gas relative permeability by a factor of two in their experiments.

2.4 Phase Behavior Studies

Production from a petroleum reservoir including a retrograde gas reservoir leads to continuous changes in its state which includes composition, pressure, temperature, quantity, properties etc. that can be grouped under the umbrella of phase behavior. Phase behavior has a direct impact again on production and thus it is a cyclical effect. Phase behavior studies have become an important part of any production process. Following is the compilation of studies carried out by various authors on phase behavior of retrograde gas reservoir fluids.

Sigmund et al. (1973) carried out a study on the effect of porous media on phase behavior. They observed that in the packing of the smallest bead size (30-40 US mesh), measured dew point and bubble point are the same as those measured in the absence of any porous media. They also

calculated the effect of curvature on phase behavior for various packings and saturations over a range of interfacial tensions. The effect was found to be insignificant except at very high surface curvatures, which were unlikely to exist in reservoirs containing connate water. The saturations obtained for the assumed differential vaporization process using previously measured volumetric and phase equilibrium data fell within saturations calculated from observed capillary structures with the assumption that all the capillary structures had equal curvature and those calculated with the assumption that they had equal volume.

Whitson (1984) have proposed a new method for calculating critical properties and acentric factor of petroleum fractions to be used as input to a cubic EOS. This method forces the EOS to match the measured values of boiling point and molar volume by adjusting critical pressure and critical temperature. Acentric factor is calculated from a correlation, which is independent of EOS & accounts for oil type using the Watson characterization factor, using boiling point and molar volume. The method was tested using PR equation of state and was claimed to match saturation data and saturation density exactly without using binary interaction coefficients.

Ahmed (1988) reviewed eight equations of state (EOS) models and compared their ability to predict the volumetric and phase equilibria of gas condensate systems. The EOS models that he compared were: (1) Peng Robinson (1976), (2) Soave Redlich Kwong (1976), (3) Schmidt-Wenzel (1980), (4) Usdin-McAuliff (1976), (5) Heyen (1981), (6) Patel-Teja (1981) (7) Kubic (1983), and (8) Adachi-Lu (1984). For his data source he used ten condensate-hydrocarbon systems with experimental PVT measurement. He concluded that Schmidt-Wenzel equation exhibited a superior predictive capability for volumetric properties of condensate systems. The Peng-Robinson was found by him to accurately represent the phase equilibrium behavior of condensate systems. For gas compressibility factor predictions, Schmidt-Wenzel and Patel-Teja both were both found to give reliable estimates by him.

Wang et al. (1989) summarized the experiences and developments in the use of EOS's for compositional reservoir simulator studies. They have highlighted on the importance of sampling, laboratory PVT experiments, number of pseudo components and tuning and gave the guidelines on getting them right.

Sarkar et al. (1991) modified Zudkevitch and Joffe method of determining parameters of an EOS and applied that to Patel-Teja (PT) EOS (1981). The modified PT EOS was validated against experimental data of gas condensate systems and compared with other leading EOS by him. His method uses binary data to determine the temperature dependency of supercritical compounds, which he states to be more suitable for gas-condensate systems as major constituents in them are at their super critical states. He has concluded that Modified Patel-Teja (MPT) EOS has improved ability to predict dew point and the retrograde condensate volume and is a superior EOS even though it doesn't use the binary interaction parameters for hydrocarbon systems.

Kokal et al. (2000) presented an experimental phase behavior data for a typical Saudi Arab gas condensate three phase (water/condensate/gas) system with an aim to quantify the effect of water on gas condensate fluid properties. Their results indicated appreciable amount of methane and carbon dioxide partitioning from gas condensate phase to the water phase, making the aqueous phase acidic. They also observed mass transfer of water into the condensate phase resulting in a decrease in gas/condensate ratio. They observed slight decrease in dew point pressure with increasing water/condensate ratio.

Elsharkawy et al. (2000) presented a new method, based on 1200 compositions of gas condensates collected worldwide, for calculating the gas compressibility factor of gas condensates at any temperature and pressure. They have presented a new simplistic mixing rule in case of known composition and specific gravity based correlation otherwise for the calculation of the compressibility factor. Their study evaluated eight methods for characterizing the plus

fraction, three mixing rules and six methods for computation of gas compressibility factor totaling one hundred and forty four methods of calculation of the compressibility factor of gas condensates. They have found that Lin-Chao correlation; SBV mixing rule as modified by Sutton and Dranchuk-Abou-Kassem resulted in the lowest errors and standard deviation with the flip side that they under estimated the compressibility factor. They claim that their new mixing rule in conjunction with Dranchuk-Abou-Kassem correlation have overall accuracy of at least 98%.

Ayyalasomayajula et al.(2002) carried out phase behavior study of hydrocarbon-water systems in presence of methanol (methanol well treatments), which is a common remedy for gas condensate well blockage, and modeled the data using both PR and SAFT equations of state. They have found SAFT to be more accurate than its counterpart PR EOS in predicting the data and this they attributed to SAFT's explicit accounting of association bonding among polar molecules. They have found that methanol-water and methanol-hydrocarbon binary interaction coefficients to play a very important role in phase behavior modeling of these mixtures using both EOS.

Lindeloff et al. (2002) presented work describing the calculation of pressure-temperature diagram of hydrocarbon-water mixture with polar interactions of aqueous compounds. They stated that their automatic calculation algorithm can generate complete three phase boundaries with a hydrocarbon liquid and an aqueous liquid including two phase and multiphase critical points. Their model calculation indicated that mixture of petroleum fluids may exhibit complex behavior including multiple three phase regions. This complexity in turn emphasized the need for thermodynamic models, which could account for hydrocarbon-water interactions.

Arcia et al. (2004) developed a new method to estimate saturation pressure based on dynamic gradient derivative obtained from in situ wellbore measurement of flowing pressure versus depth with field examples from east Venezuela. A dispersion of less than 1% was obtained by them between laboratory derived saturation pressure and the dynamic gradient results. They claim to

have successfully applied this method to validate laboratory PVT analysis and for EOS modeling of condensate systems. Though their method could be used for black oil, volatile oil as well as gas condensates, it could however be used only for cases where reservoir and bottom hole flowing pressure are above the saturation pressure.

Pedersen et al. (2004) presents phase equilibrium data for the mutual solubility of brine and a gas condensate mixture at temperatures ranging from 35⁰C to 200⁰C and pressures of 700 bar and 1000 bar. Their phase compositions were compared with compositions of the same gas condensate with pure water measured at the same conditions. They modeled their experimental data with SRK and PR EOS with Huron and Vidal mixing rule. They observed that the dissolved salts reduced the gas solubility in water. They also observed that the water content in hydrocarbon gas in equilibrium with a water phase containing salts can be quite significant at high pressures and temperatures and is only slightly affected by a salt content of around 3.5 mole%.

Bang et al. (2006) carried out constant composition expansion experiments to measure the phase behavior of hydrocarbons-water-methanol mixtures upto a temperature of 300⁰F. They also measured the effect of temperature, pressure and water and methanol concentration on the phase behavior. Peng Robinson Equation of state along with Peneloux volume correction and van-der-Waals as well as Huron-Vidal mixing rules gave successful validation of the data generated using the hydrocarbon-water-ethanol mixtures. They tuned binary interaction parameters to fit the data and found that the binary interaction parameters showed a linear trend with temperature. They observed that the addition of methanol increased the liquid volume fraction and the dew point pressure and addition of water though resulted in the formation of a third phase but the ratio of hydrocarbon liquid volume to vapor phase volume and dew point pressure changed very little. Addition of methanol to hydrocarbon-water mixtures resulted in reduction of dew point

pressure and significant increase of aqueous phase volume but on the other hand addition of Iso propanol increased the hydrocarbon liquid phase volume fraction rather than aqueous phase volume fraction.

Thomas et al. (2006) have reviewed and proposed techniques for sampling and characterization for minimizing the errors involved in these steps. They have concluded that multi-rate sampling is the best method to use in sampling fluids since the liquid yield changes as the function of rate. They stressed of the need to have prior information of the condensate-gas ratio as a function of the flow rate and the samples used in recombination should correspond to the highest liquid-yield sample set. Bottom hole sampling was advised to address any concerns of liquid-solid separation. The importance of path-dependence was shown to be significant when creating equilibrium phases below saturation pressure for use in quantifying phase interference. The differences in API gravity of liquids in solution were quantified to be as much as 10 degrees with MW differences over 110 Daltons.

2.5 Surfactants

Surfactants, short for surface active agents, are polar, amphiphilic molecules (presence of both hydrophilic head group as well as hydrophobic tail groups) that are classified on the basis of the charge of the hydrophilic group present in them. The four categories³⁸ are:

- I. Anionic: Hydrophilic group carries a negative charge such as carboxyl ($\text{RCOO}^- \text{M}^+$), sulfonates ($\text{RSO}_3^- \text{M}^+$), or sulfate ($\text{ROSO}_3^- \text{M}^+$).
- II. Cationic: Hydrophilic group carries a positive charge such as quaternary ammonium halides ($\text{R}_4\text{N}^+\text{X}^-$).
- III. Nonionic: Hydrophilic group carries no charge but derives its water solubility from highly polar groups such as polyoxyethylene group such as $(-\text{OCH}_2 \text{CH}_2\text{O}-)$, sugars or similar groups.

IV. Amphoteric (or Zwitterionic) : wherein molecule carries a positive and negative charge on the principal chain as opposed to counter ion (M^+ or X^-) such as sulfobetaines ($RN^+(CH_3)_2 CH_2 CH_2 SO_3^-$).

Surfactants are known to act on the interfaces between immiscible oil/water/gas phases as well as their interfaces with rock surfaces. They tend to decrease their interfacial tensions between the phases by aggregating at the interfaces while orienting their hydrophilic head groups and hydrophobic tail groups perpendicular to the interfaces and thereby bonding the phases together.

Trogus et al. (1977) carried out surfactant adsorption studies with a class of polyoxyethylenated nonylphenols surfactants. They concluded that relative adsorption levels for non-ionic and anionic surfactants could be modeled using a second order reversible rate expression that reduced to a Langmuir type adsorption isotherm at equilibrium. They found that the adsorption levels for the non-ionics and anionics to be of comparable magnitude. Adsorption increased sharply as the concentration increased and leveled off to a nearly constant value at the critical micelle concentration for both the anionics and the non-anionics. They noted that the level of adsorption decreased with increased molecular weight for the non-ionics, which was opposite to what was seen with the anionics. When adsorption was based on unit surface area, the plateau values were independent of adsorbent and type of experiment for the non-ionic surfactants. The adsorption of the non-ionic surfactants was ascribed to hydrogen bonding mechanism with the terminal OH group interacting with appropriate sites.

Asar et al. (1988) carried out coreflood studies with methane/propane system to determine the effect of IFTs on gas/oil relative permeabilities. IFT was varied from 0.03 to 0.82 dynes/cm by changing the pressure or the composition of the experiment near the critical region of the methane/propane system at a constant temperature of 70°F. They observed that the curves of individual relative permeabilities (k_{rg} and k_{ro}) vs. gas saturation tend to straighten and approach

the 45° line as IFT approached zero. Relative permeability to oil decreased more rapidly compared with the relative permeability to gas as IFT was increased. They also observed that the residual gas and oil saturations were higher with higher IFTs. The gas saturation at which individual relative permeability curves intersected was higher as the IFT decreased indicating a decrease in the oil-wet character of the system. Saturation hysteresis was not observed to be significant at intermediate IFTs in this case. They have further opined that the relative gas and oil permeabilities for gas condensate reservoirs corresponded to a normal gas/oil system except at conditions close to critical. They also concluded that at low IFTs near the critical point, liquid could flow at low liquid saturations in condensate reservoir.

Kwok et al. (1993) conducted an experimental study to examine the propagation with adsorption of an anionic surfactant in un-fired Berea sandstone cores. They also studied the effects of sodium chloride concentration, pH, flow rate, surfactant concentration and the presence of a liquid crystal phase on the rate of surfactant propagation. They concluded that at low surfactant concentrations, the effect of sodium chloride concentration on surfactant concentration and propagation was significant with increased surfactant adsorption as the sodium chloride concentration increased. By increasing the pH of the surfactant slug, the surfactant loss was reduced by 30%. They also observed that, at a given sodium chloride concentration and surfactant concentration, the surfactant loss decreased as injection flow rate increased. They observed the formation of a liquid crystal phase at high surfactant concentration and a narrow range of sodium chloride concentration. This phase resulted in a higher apparent viscosity, increased pressure drop and significant surfactant retention in the core attributed to the formation of viscous fingers at the tail of the surfactant slug.

Mannhardt et al. (1994) carried out adsorption studies on representatives of four classes of surfactants suitable for foam flooding on Berea sandstone at different conditions of temperature

and salinity. Anionic surfactants AOS 1416 and IOS 1518 did not adsorb from low salinity (0.5% NaCl) brine. Adsorption of both surfactants increased with increasing brine salinity and divalent ion content. Experiments with anionic surfactant LXS 810 showed that ion exchange of clays and surfactant micelles could cause precipitation in the porous media, even when the surfactant was completely soluble in the injected brine. The amphoteric surfactant Stepanflo 60 was the most soluble of the tested surfactants and adsorbed much more strongly on sandstone than the anionic surfactants. Within the anionic surfactants they observed increasing adsorption with decreasing surfactant solubility.

Tang et al. (2002) carried out relative permeability studies on Berea and Chalk cores before and after alteration of wettability from strong liquid wetting to intermediate gas wetting for gas/oil and gas/water fluids using polymers FC-722 & FC-759. They used n-decane as the oil phase, 0.2% (wt) NaCl brine as the water phase and air as the gas phase for their experimentation. They observed significant liquid phase mobility as a consequence of intermediate gas wettability.

Hirasaki et al. (2004) worked on the surface chemistry of oil recovery from fractured oil-wet carbonate formations. They observed that calcite, which is normally positively charged at neutral pH, could be made negatively charged through the presence of $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$ in the brine. The wettability of the crude-oil/brine on a calcite plate was a function of aging time. After 24 hours, the plate was oil-wet regardless of whether the aging in crude oil was at room temperature or at 80°C. The degree of wettability alteration with alkaline surfactant system that they observed ranged from preferentially water to intermediate wet and was a function of the prior aging temperature in crude oil. They demonstrated oil recovery from oil-wet dolomite cores by spontaneous imbibition with an alkaline anionic surfactant solution.

Seethepalli et al. (2004) investigated the interactions of dilute alkaline anionic surfactant solutions with crude oil on carbonate mineral surfaces. They conducted wettability, phase

behavior, interfacial tension as well as adsorption experiments. They observed that the anionic surfactants (SS-6656, Alfoterra-35,36,37,38) could change the wettability of the calcite surfaces to intermediate water wet condition as well as or better than the cationic surfactant (DTAB with a west Texas crude oil in presence of Na_2CO_3). The anionic surfactants were also observed to lower the IFT with a west Texas crude oil to very low values. They observed that the adsorption of sulfonate surfactants was reduced significantly by addition of Na_2CO_3 .

Fahes et al. (2007) conducted core flood studies on sandstone cores of high and low permeability range upon wettability alteration to intermediate gas wetting at a high temperature of 140°C . They have concluded that wettability could be permanently altered from liquid-wetting to intermediate gas-wetting at high reservoir temperature of 140°C . Wettability alteration had a substantial affect on increasing liquid mobility as well as gas productivity at reservoir conditions. They did not find the effect of wettability alteration on the absolute permeability of the system.

Panga et al. (2007) tested 41 chemicals using contact angle and imbibition test to select appropriate chemicals for flow tests to analyze its effect on removing water and condensate blockage permanently. The chemicals were observed to have altered the wettability of the cores studied and have recommended chemical A5 for water block prevention when diluted in brine. They however found that the same chemical when dissolved in organic solvents like methanol and IPA and injected at high temperature gave poor cleanup, which they suspected may be because of the precipitation formed at the injection surface. This precipitation was not observed when the same system was used at low temperature.

Xu et al. (2008) conducted experimental measurements of IFT and contact angle at high pressure and high temperatures to determine the effect of surfactants on oil/water interfacial tension and wettability in crude-oil/brine/rock systems at reservoir conditions. Drop shape analysis (DSA) and Dual drop dual crystal (DDDC) techniques were used for measurement of IFT and contact

angle respectively on live oil as well as stock tank oil at reservoir conditions. They observed a dynamic IFT behavior between crude oil and brine, which they ascribed to the presence of polar components such as asphaltenes in the crude oil or added surfactants and adapted a four-stage model to describe the process. They observed that all concentrations of anionic surfactant (ethoxy sulfate) altered the wettability of strongly oil-wet stock-tank-oil/brine/dolomite system to a less oil-wet state. The anionic surfactant was also observed to alter the wettability of initially weakly water-wet live-oil/brine/dolomite system to a strongly oil-wet state. In case of non-ionic surfactant (ethoxy alcohol) they did not see any significant influence on the strongly oil-wet stock-tank-oil/brine/dolomite system, however, the same surfactant altered the wettability from water wet to intermediate wet in case of live-oil/brine/dolomite system.

Kumar et al. (2008) studied the mechanisms of wettability alteration by crude oil components and surfactants. Contact angles were measured on mineral plates treated with crude oils, crude oil components and surfactants and those mineral surfaces were also studied with atomic force microscopy. They concluded that the wettability was controlled by the adsorption of asphaltenic components as the force of adhesion for minerals aged with just the asphaltene was similar to that of the whole oil. Both anionic and cationic surfactants were found to help imbibe water into initially oil wet capillaries. Among the surfactants studied by them, the imbibition was the fastest with Alf-38 and slowest in case of DTAB. Force of adhesion and contact angle measurements by them showed greater wettability alteration potential by the anionic surfactants compared to the cationic ones studied by them. However, the water imbibition rate did not increase monotonically with the increase in the surfactant concentration.

Zheng et al. (2010) measured both the spreading coefficient and wettability to characterize the influence of anionic and nonionic surfactant on interfacial behavior. The contact angles were measured using Dual Drop Dual Crystal (DDDC) technique interfacial tensions were measured

using Drop Shape Analysis (DSA) and Capillary rise technique. The experiments were performed at ambient conditions by using stock tank condensate sample, methane, synthetic reservoir brine and quartz substrate and test indicated their system to be strongly oil wet with an advancing contact angle of 152° . Though they obtained positive spreading coefficient for condensate/brine system with or without surfactant, it decreased after surfactant application showing oil recovery still enhanced from surfactant usage in their strongly oil-wet system. They reported wettability alteration from strongly oil wet to intermediate oil wet using anionic surfactant, however, not alteration was noticed with nonionic surfactant.

CHAPTER 3: EXPERIMENTAL APPARATUS AND PROCEDURE

3.1 Experimental Apparatus

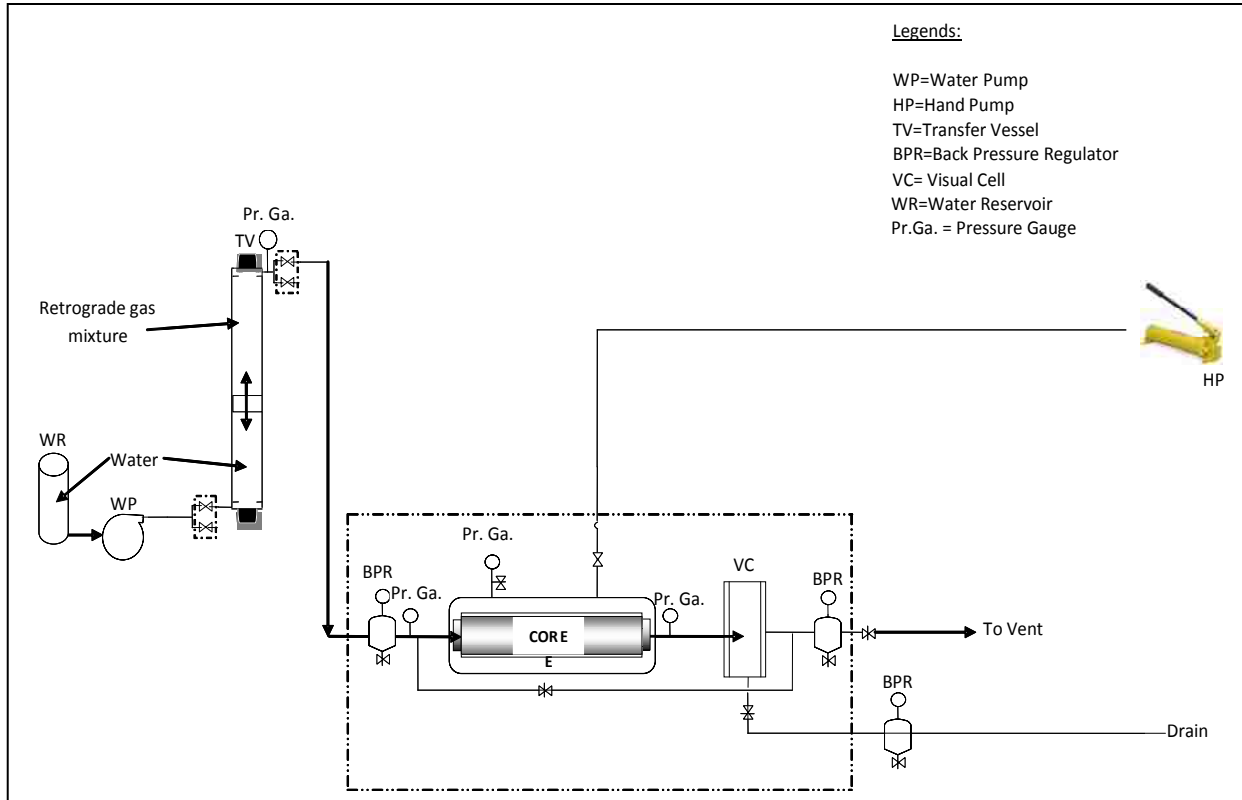


Figure 3.1 Schematic of the experimental apparatus

Figure 3.1 shows the schematic of the experimental apparatus. The photograph of the same is shown in figure 3.2. This apparatus has been designed and built in house by procuring the components listed in the section below from their respective vendors. The apparatus is capable of withstanding reservoir conditions of temperatures (250°F) and pressure (5000 psi). The design of the apparatus aimed to effect retrograde condensation within the core system by the process of dynamic flashing. This has been achieved by means of two back pressure regulators (BPR) connected at the upstream and downstream ends of the core with the upstream BPR set above and the downstream BPR set below the dew point pressure of the gas mixture. A relief valve was incorporated along with the other valves assembly in the accumulator for it to operate safely under the prevailing high pressure conditions. The relief valve was set at 4400 psia so as to

protect the accumulator, which is rated at 5000 psia. A vent connection system was also put in place to take the highly inflammable hydrocarbon gases out of the laboratory. A visual cell was also connected in line to be able to observe the condensate being carried over by the gas. Highly precise digital test gauges were used with the system. The components of the apparatus are as listed below:

- A. **Core holder:** A Core Holder from M/s Phoenix instruments, rated for 5000 psi model LSU-HAS-2x12-5k-02.
- B. **Back pressure regulator:** Back pressure regulators from M/s Tescom rated for 0-6000 psi, model 26-1700 series.
- C. **Liquid pumps:** A constant rate water pump with flow accuracy of 0.001 uL from GMI Inc., rated for 12 ml/min at 6000 psi, model Lab Alliance Series 1500 and a high flow rate high pressure liquid pump from Maxpro Technologies, rated for 12470 psi, model PP 72 SHL were used.
- D. **Gas hand pump:** A piston screw hand pump from M/s Ruska rated for 10000 psi.
- E. **Flow meter:** An industrial gas mass flow meter from M/s Brook's instruments, rated 0-5000 sccm & 4500 psi, model 5860i.
- F. **Accumulators:** High temperature and high pressure accumulators (transfer vessels) from M/s Temco rated for 5000 psi, models CFR-50-200-HC-T-350, CFR-50-200-SS-350.
- G. **Digital pressure gauges:** Digital pressure gauges from Ashcroft rated for 0-5000 psi and 0-7000 psi, model 2089.
- H. **Visual cell:** High temperature and high pressure visual cell rated for 6000 psi and 400⁰F.
- I. **Relief Valve:** High pressure relief valves from Swagelok set and locked at 4400 psia using metal clip.

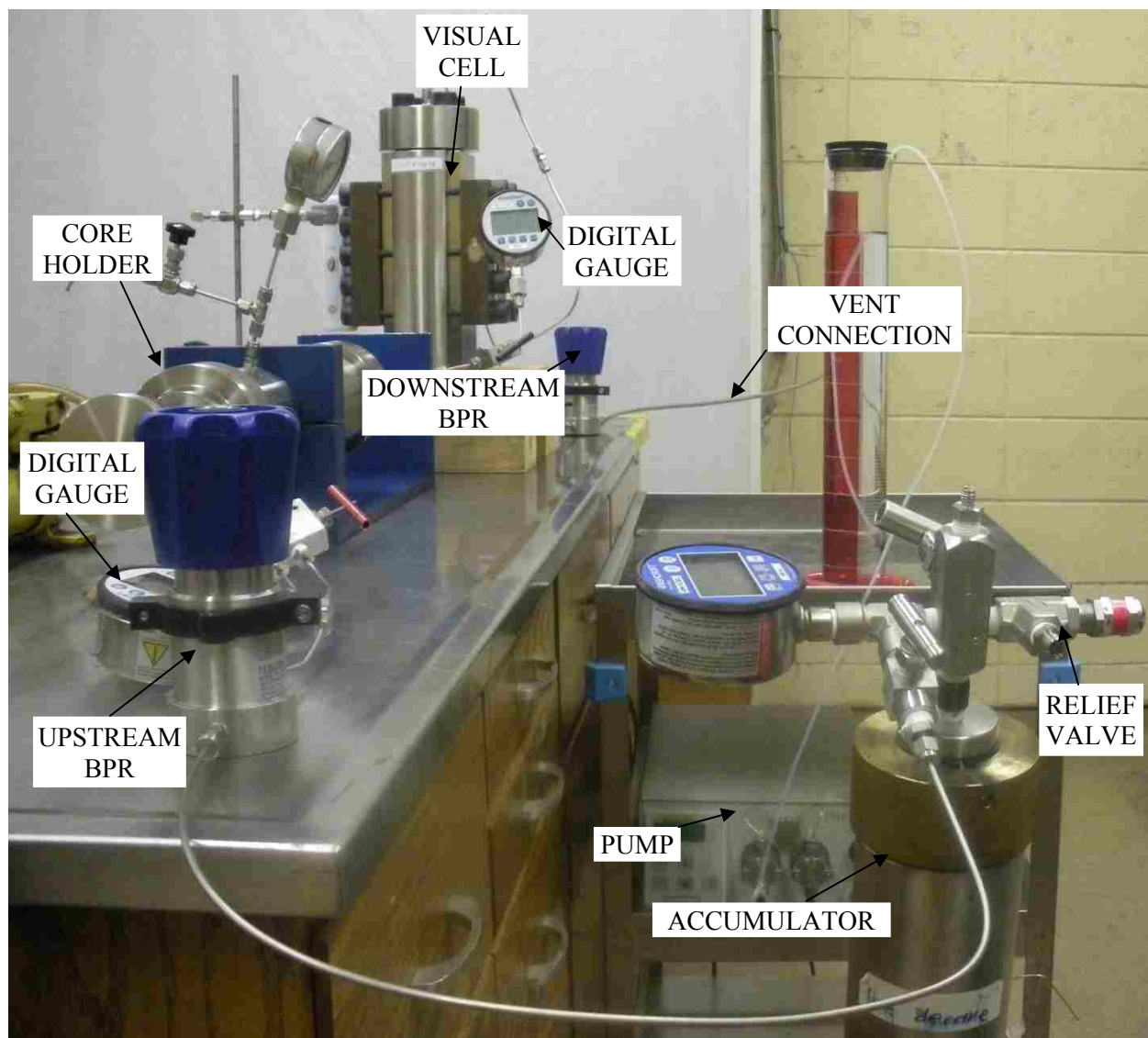


Figure 3.2 Picture of the experimental apparatus

3.2 Experimental Procedure

3.2.1 Core Preparation

Parker sandstone cores, 5-10 mD, were chosen for the experiment as their permeability were low enough to allow noticeable pressure drop across the core required for in-situ retrograde condensation. Parker sandstone core of dimensions 2" by 12" was wrapped with Teflon tape and put in 2" Viton sleeve so as to prevent the brine from contacting the hydraulic oil in the annulus.

This wrapped core was placed inside the core holder taking care not to damage the “O” rings in the core holder body.

3.2.2 Saturation of the Core

The core was saturated by pumping brine at a very low flow rate, 30 ml/hr, into the vacuumed core and the pressures at both the ends of the core were noted. The level in the measuring cylinder (pump reservoir) was also noted with time. The point at which the pressures at both ends of the core equalized indicated the pore volume of the core. Brine was pumped into the saturated core at three different flow rates of 120ml/hr, 240ml/hr and 480ml/hr and the corresponding stabilized pressures were noted to calculate the absolute permeability of the core. The core was then kept saturated at 1000 PSI for 48 hrs.

3.2.3 Establishing Irreducible Water Saturation (S_{wi})

The core system was placed vertically and methane gas was injected at a very low flow rate, 20 ml/hr, with the brine displaced from bottom until no more brine came out. The volume of brine drained was noted. This enabled the calculation of irreducible water saturation in the core.

3.2.4 Artificial Retrograde Gas Condensate Mixture Preparation

A proper retrograde gas is vital to the success of the experiment. Because of understandable difficulties in the procurement of retrograde gas samples from the field, an effort was made in this study to get a suitable retrograde gas mixture by artificially combining the respective constituents in an appropriate proportion. In order to avoid the purchase of a big and expensive oven, the mixture needed to have the retrograde region of sufficient liquid dropout at the ambient temperature. CMG-developed PVT software WinProp was used to identify the right composition of the gas mixture that exhibited the retrograde condensation behavior at ambient temperature and reasonable dew point pressure. The Peng-Robinson EOS within the WinProp software was used for phase envelope calculation. While trying to formulate the mixture composition, two

points were kept in mind: (1) First the phase envelope must have a retrograde region. (2) Critical point should be as far down as possible of the phase envelope so that the retrograde condensation occurs at ambient temperature. It was noted that the larger differences in the molecular sizes of the components caused very large critical pressures. Pure normal alkanes from methane to decane were considered for the purpose. Various combinations of the components from methane to decane were considered with different compositions and their respective phase envelopes generated using CMG WinProp. To illustrate the procedure followed while preparing the composition Table 3.1 shows the three compositions of methane, n-butane and n-heptane. Keeping methane composition fixed at 85%, the mole percentage of n-Butane and n-Heptane were varied and the phase envelopes generated are shown in Figures 3.3 to 3.5. It can be seen from the phase envelopes that, as the mole percentage of the heavier component, heptane, increased the critical temperature increased from 55 to 95°F and the phase envelope also widened. It is seen from these phase envelopes that just by varying the composition of one single component by a unit mole percentage can drastically change the entire phase properties of the mixture. Hence, utmost care is called for both the design and preparation of the recombinant retrograde gas mixture.

Table 3.1 Artificial condensate compositions

Gas Mixture	Component	Mole Percentage (%)	Mole Percentage (%)	Mole Percentage (%)
1	Methane	85	85	85
2	n-Butane	5	4	3
3	n-Heptane	10	11	12

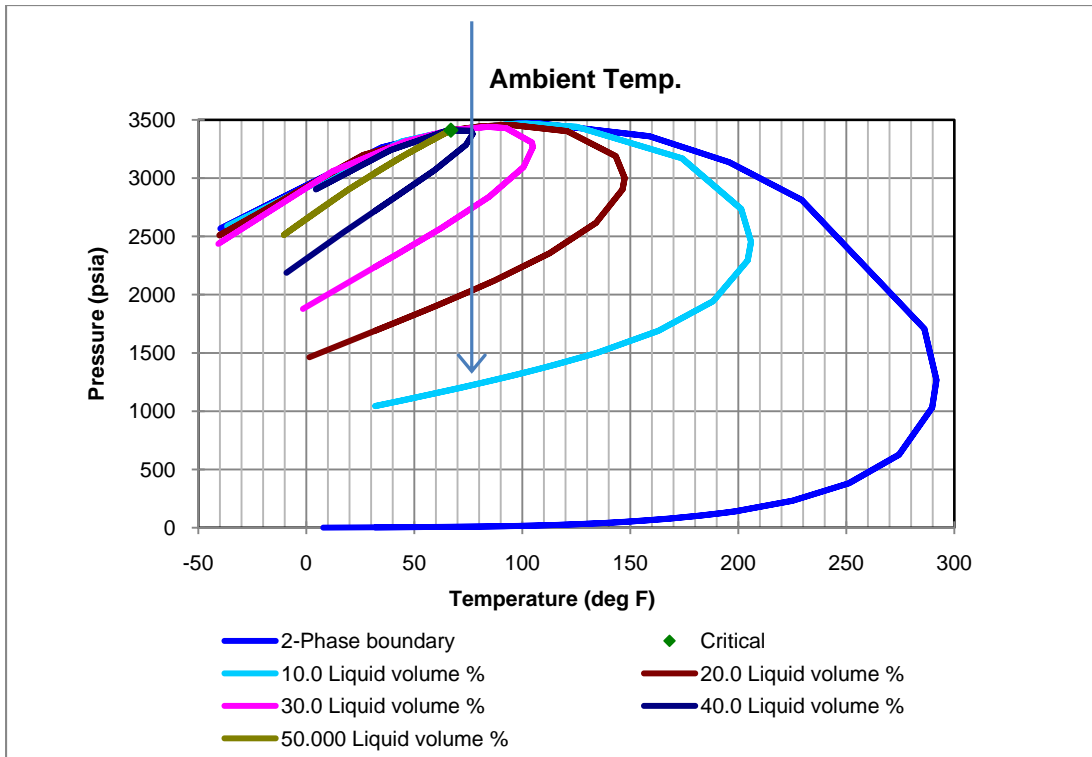


Figure 3.3 PT phase diagram for the composition 85% C1, 5% nC4, 10% nC7-Mixture 1

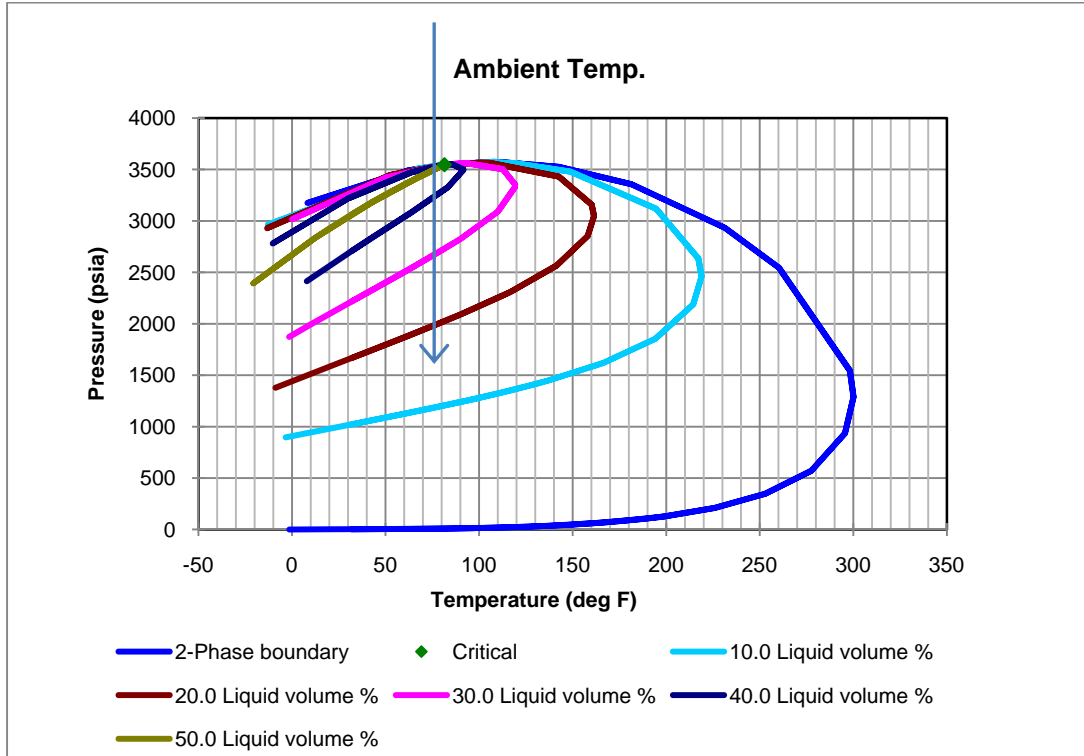


Figure 3.4 PT phase diagram for the composition 85% C1, 4% nC4, 11% nC7-Mixture 2

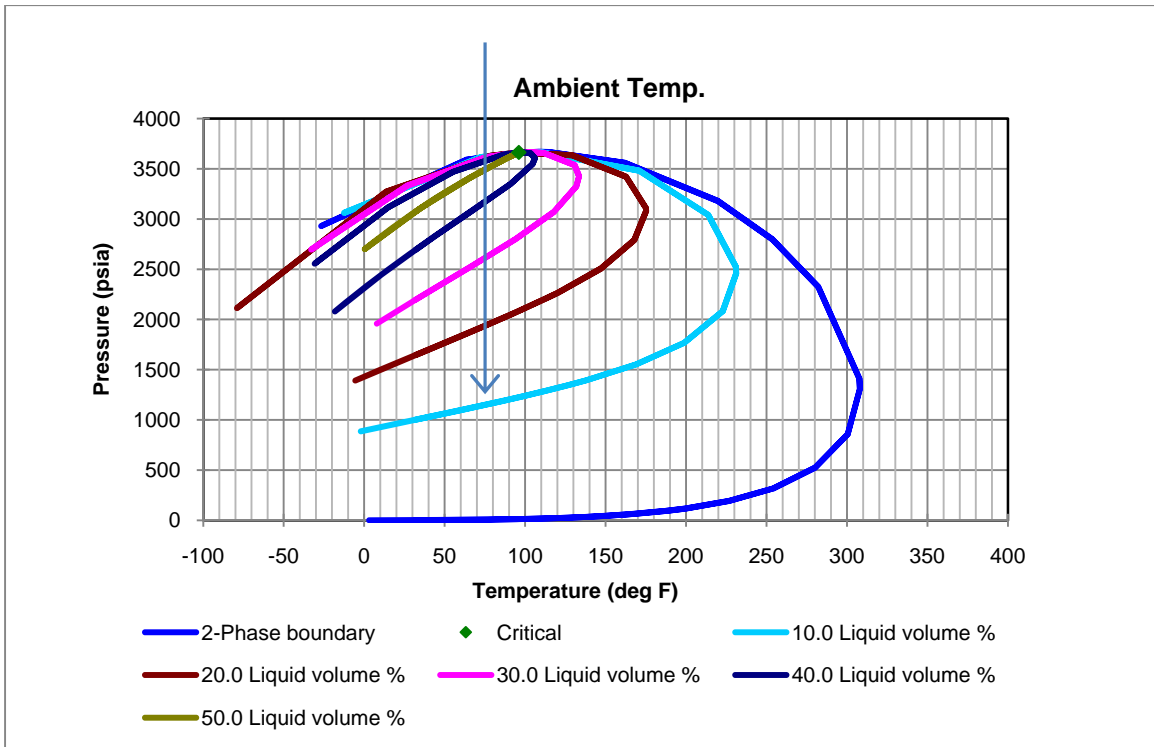


Figure 3.5 PT phase diagram for the composition 85% C1, 3% nC4, 12% nC7-Mixture 3

Table 3.2 lists the composition of the final retrograde gas mixture. The PT phase diagram for the retrograde gas mixture is given in Figure 3.6. The critical temperature obtained using this composition was ~ 53 °F and the cricondentherm was at 280°F. Hence this mixture exhibited retrograde condensate behavior at ambient temperature as required for the planned experimentation. The retrograde region was through the ambient temperature. Figure 3.7 gives the liquid drop out curve for the mixture calculated using Peng Robinson EOS.

Table 3.2 Artificial condensate composition

Sl. No.	Component	Mole Percentage (%)
1	Methane	85
2	n-Butane	6
3	n-Heptane	9

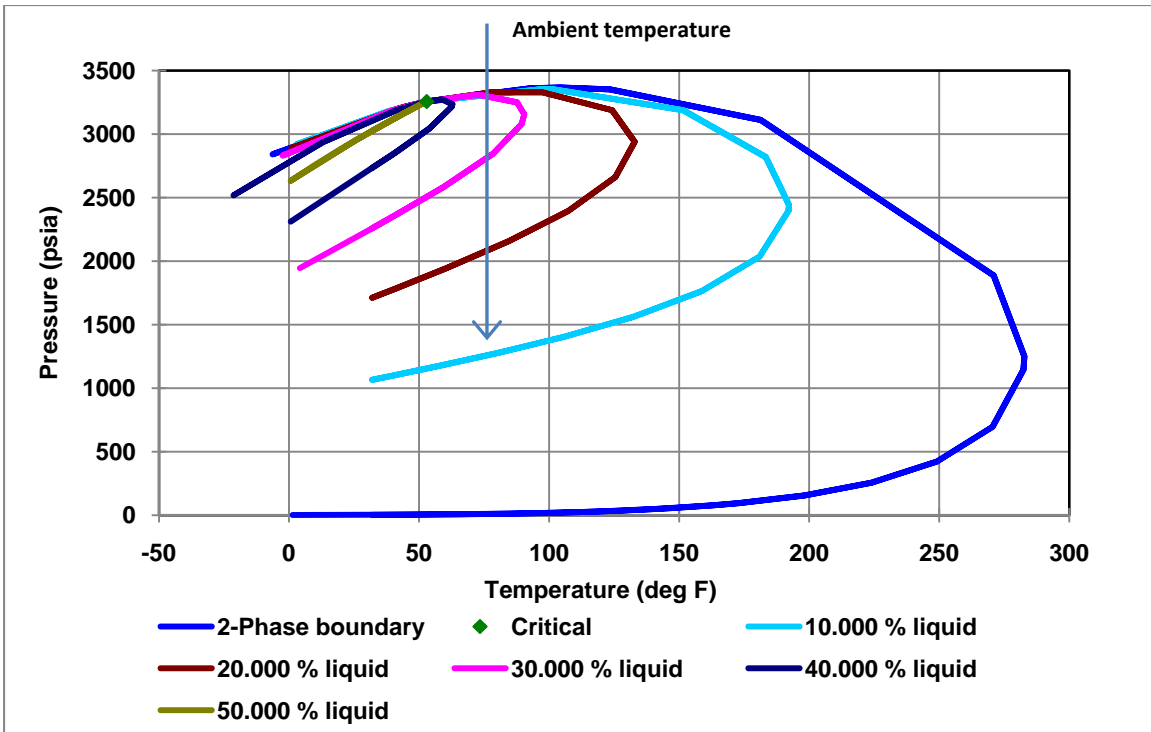


Figure 3.6 PT phase diagram for the retrograde gas

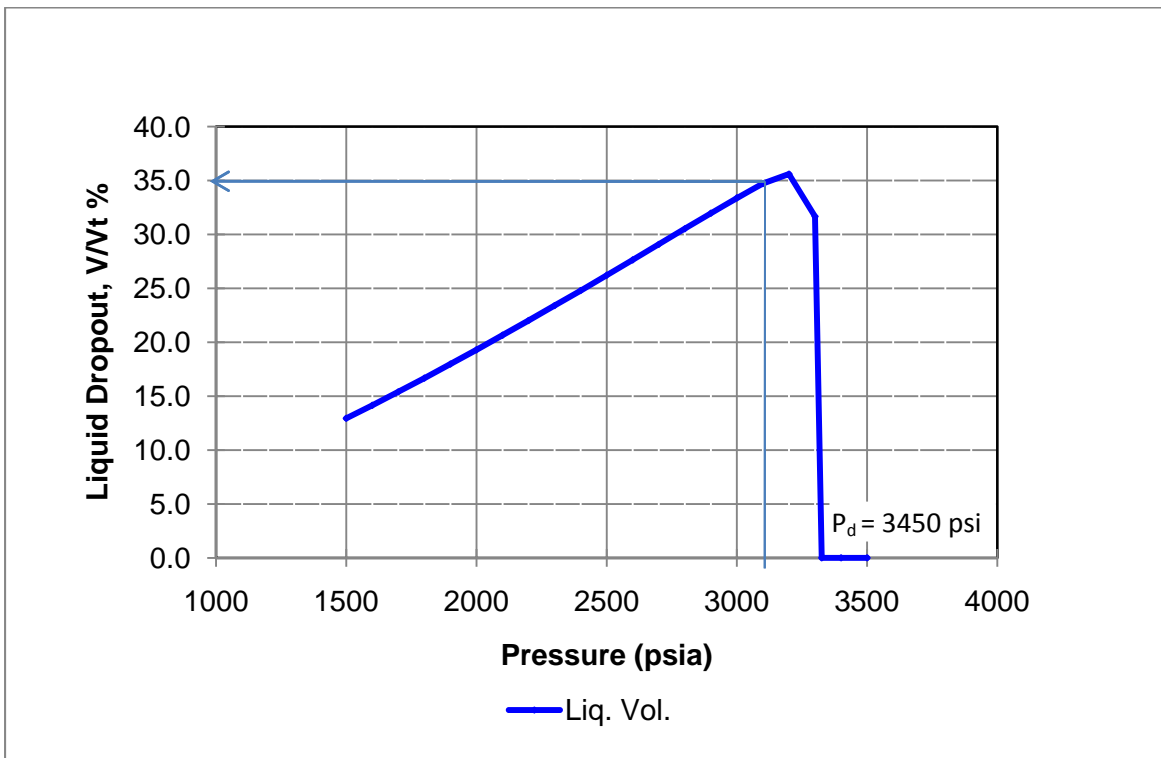


Figure 3.7 Liquid drop out curve calculated using PR EOS at 73°F

For the preparation of artificial condensate gas, high purity methane (99.99 %) and normal Butane (99.999%) were obtained from Airgas Co. and high purity normal Heptane (>99.95%) was obtained from Fisher Scientific. The mixture was prepared on volume (mole) basis in an accumulator rated for 7000 psi. The three components were separately transferred to the accumulator in metered quantity by first transferring to a piston screw hand pump from Ruska rated for 10000 psi. This was done so as to have finer control in administering the required amount of the particular component into the accumulator as the hand pump was accurate to 100th of an ml. It was taken care to clean the hand pump and the connecting tubing and valves thoroughly with acetone and then subsequent vacuuming before the next component was added. Utmost care was taken to double check the fittings for any possible leakage. After the transfer of all the components the accumulator was rocked to mix all the components. The pressure of the accumulator was then raised to above dew point pressure and kept for 12-15 hours for the single phase mixture to equilibrate. The accumulator was again rocked before starting the core flood experiments.

3.2.5 Core Flood Procedure of Gas Mixture

Prepared retrograde gas was flooded through the core both above and below the dew point pressure. For the retrograde gas flood above the dew point pressure, the upstream (of the core) back pressure regulator (BPR) was set at 3700 psi and the downstream BPR was set at 3500 psi. The mixture was pumped at three different flow rates (120ml/hr, 240ml/hr, and 480 ml/hr) and the pressure drops across the core were noted.

For the retrograde gas flood below the dew point, the downstream BPR setting was changed to 3100 psi keeping the upstream BPR setting unchanged. Again the mixture was pumped at the same three different flow rates and the pressure drops noted. At this downstream pressure the retrograde mixture flashes downstream of the upstream BPR and the mixture becomes a two

phase fluid. This dynamic flashing technique mimicked the actual reservoir phenomena of retrograde condensation.

3.2.6 Subsequent Retrograde Gas Floods

For subsequent retrograde floods, **steps 3.2.1 – 3.2.5** were repeated with the exception that saturation was carried out with brine containing different concentrations of surfactant. Different surfactant concentrations used were 1000 ppm, 2000ppm and 5000 ppm. Surfactant used was an anionic surfactant Alfoterra® 123-4S, provided by M/s Sasol surfactants. Alfoterra® 123-4S belongs to class of surfactants known as alkyl propoxy sulfates and has 12-13 number of hydrophobe carbon and 4 moles of propoxy unit. Its mono branched alkyl hydrophobe allows for greater interaction with the oil phase while maintaining good solubility. This surfactant has been found to develop intermediate wettability in the core from a concentration as low as 500 ppm from DDDC measurements by Zheng et.al (2010). The spreading coefficient was also found to be positive with this surfactant.

CHAPTER 4: RESULTS AND DISCUSSION

Sections 4.1 through 4.4 discuss different cases given in Table 4.1. For all the cases listed in Table 4.1, coreflood of the gas condensate mixture was run both above and below the dew point pressure for the retrograde gas mixture. Figures 4.1 through 4.5 show the pressure drop versus time for the three flow rates 120ml/hr, 240ml/hr and 480ml/hr that were used in the experimentation. Also shown in these figures is the upstream pressure of the core system observed during the experiment. It is noticed that the pressure drop is the lowest for the above dew point pressure runs. This is because of the fact that the mixture is a single phase gas and no retrograde condensation takes place since the pressure is above the dew point pressure. There is slight undulation in the pressure response and this may be because of the formation and breakage of ice crystals due to Joule Thompson cooling effect as the gas mixture passes across the back pressure regulator. The relative permeability value for the gas in the above dew point pressure case is the highest, being 0.359. Figure 4.2 gives the relative permeability chart for this case. Table 4.2 lists the initial core properties for a typical core. The permeability of the gas is severely impaired by the presence of high irreducible water saturation (47.12%) in the tight Parker Sandstone core (5-10 mD).

Table 4.1 Different cases considered in experimentation

Sl. No.	Cases	Description
1	Case I	Saturation with Brine without Surfactant
2	Case II	Saturation with Brine containing 1000 ppm Surfactant
3	Case III	Saturation with Brine containing 2000 ppm Surfactant
4	Case IV	Saturation with Brine containing 5000 ppm Surfactant

Table 4.2 Core properties for a typical core

Sl. No.	Item	Description/Value
1	Core	Parker sandstone
2	Dimensions of the core	2" diameter X 12" length
3	Bulk volume of the core	617.78 ml
4	Pore volume of the core	104 ml
5	Porosity	16.83%
6	Irreducible water saturation	47.12%
7	Absolute permeability of the core	8.64 mD

4.1 Saturation with Brine without Surfactant (i.e. 0 ppm Surfactant Concentration)

Figure 4.1 shows the comparison of pressure drops above and below the dew point pressure for the case of brine without surfactant. Upstream pressure for the core system is also shown in the figure. It can be seen that pressure drop for the below dew point case is fairly higher than that of above dew point case, demonstrating the flow impediment caused by the liquid condensate dropout in the core due to retrograde condensation. This test clearly demonstrates the occurrence of in situ retrograde condensation and the restricted flow for the gas condensate mixture. As can be seen from the graph, there is continued rise in pressure drop with a low slope even at the same flow rate. This is because of the fact that more and more amount of condensates are being formed as the retrograde gas mixture undergoes condensation below dew point and this condensate tends to accumulate in the core system leading to rising trend in pressure drop. Figure 4.2 gives the relative permeability calculation chart for the single phase gas flow at pressure above the dew point pressure. The relative permeability value got for the single phase gas flow above dew point was 0.359.

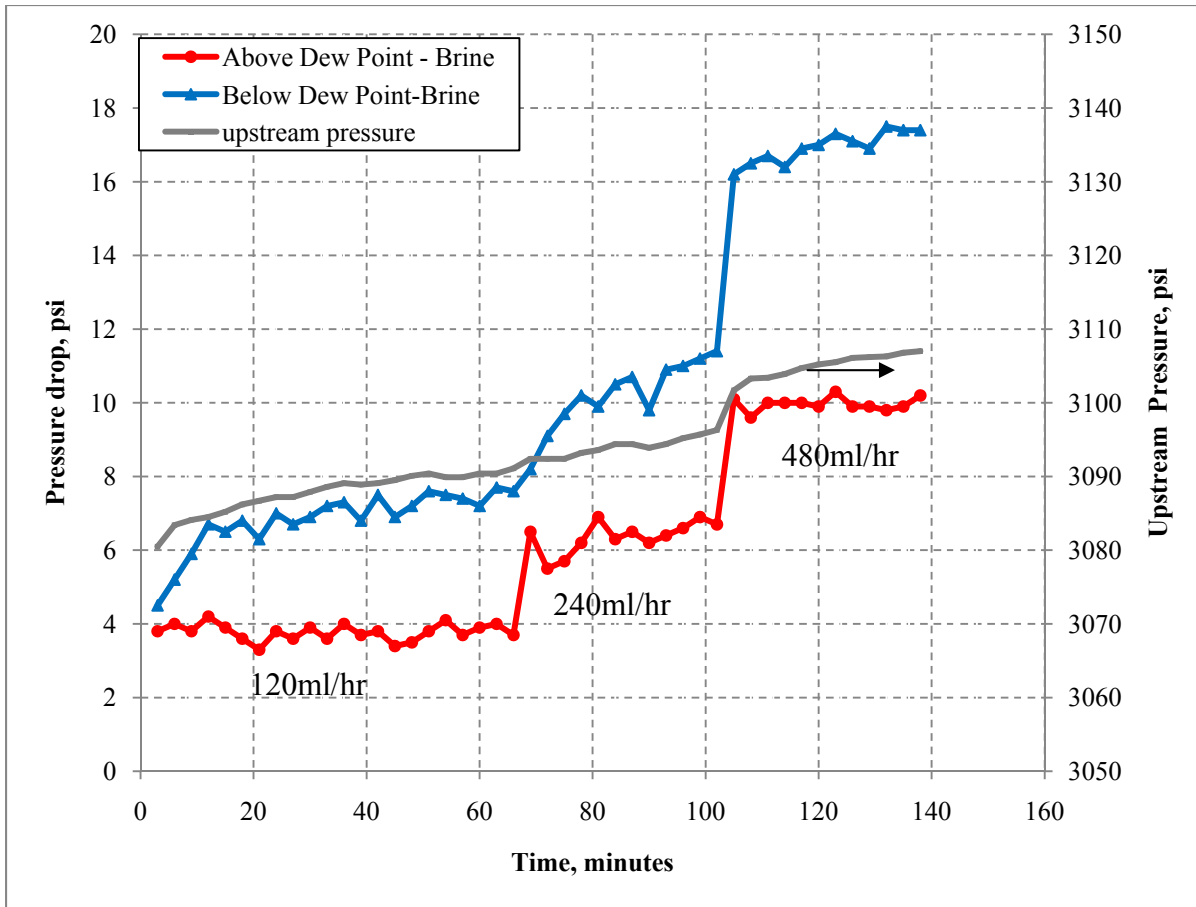


Figure 4.1 Pressure drop above and below dew point for brine without surfactant

The gas relative permeability value for this case of brine without surfactant is calculated to be 0.210. Figure 4.3 gives the relative permeability calculation chart for this case of brine without surfactant. It is noticed that there is a reduction in relative permeability of over 40 percent from the above dew point case, wherein the relative permeability was 0.359. This relative permeability reduction leads to severe productivity loss observed with gas condensate wells. An example economic analysis is given at the end of this chapter incorporating these values of relative permeability reduction. The economic analysis clearly underscores the loss in revenue to the petroleum industry as a result of this problem of condensate banking. The following sections show the improvement to the relative permeability brought about by surfactant.

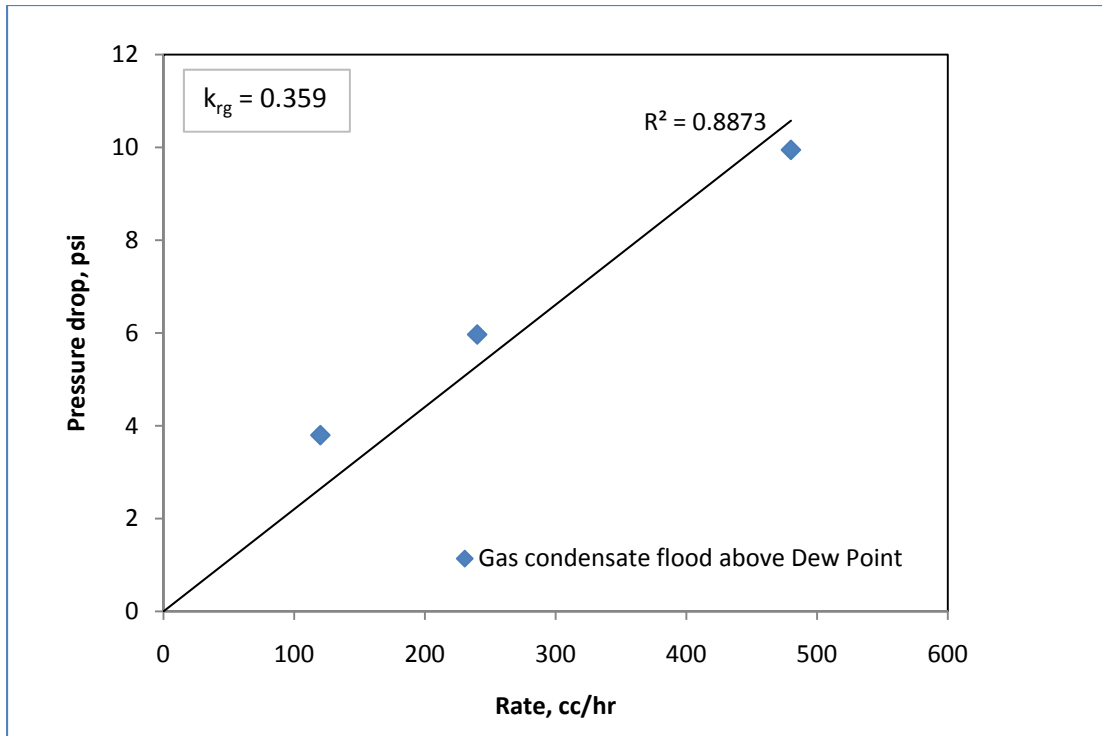


Figure 4.2 Relative permeability above dew point pressure

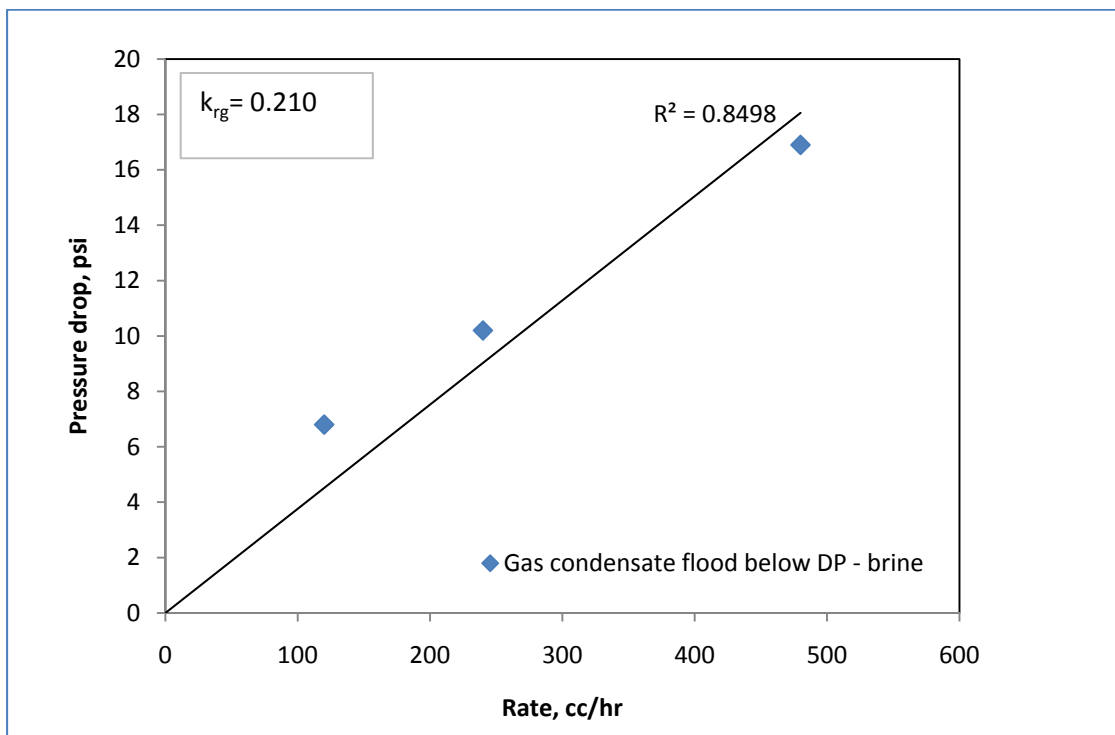


Figure 4.3 Relative permeability below dew point – brine without surfactant

4.2 Saturation with Brine Containing 1000 ppm Surfactant Concentration

Figure 4.4 shows the comparison of pressure drops above and below the dew point pressure for the 1000 ppm surfactant case with that of brine without surfactant case. There is improvement with respect to pressure drops from the brine without surfactant case but it is not quite substantial. The gas relative permeability in this 1000 ppm surfactant case is 0.221 (figure 4.5), which is still 38 percent lower than the above the dew point case. Thus 1000 ppm surfactant is not able to significantly alter the flow behavior of the gas mixture than the brine without surfactant case.

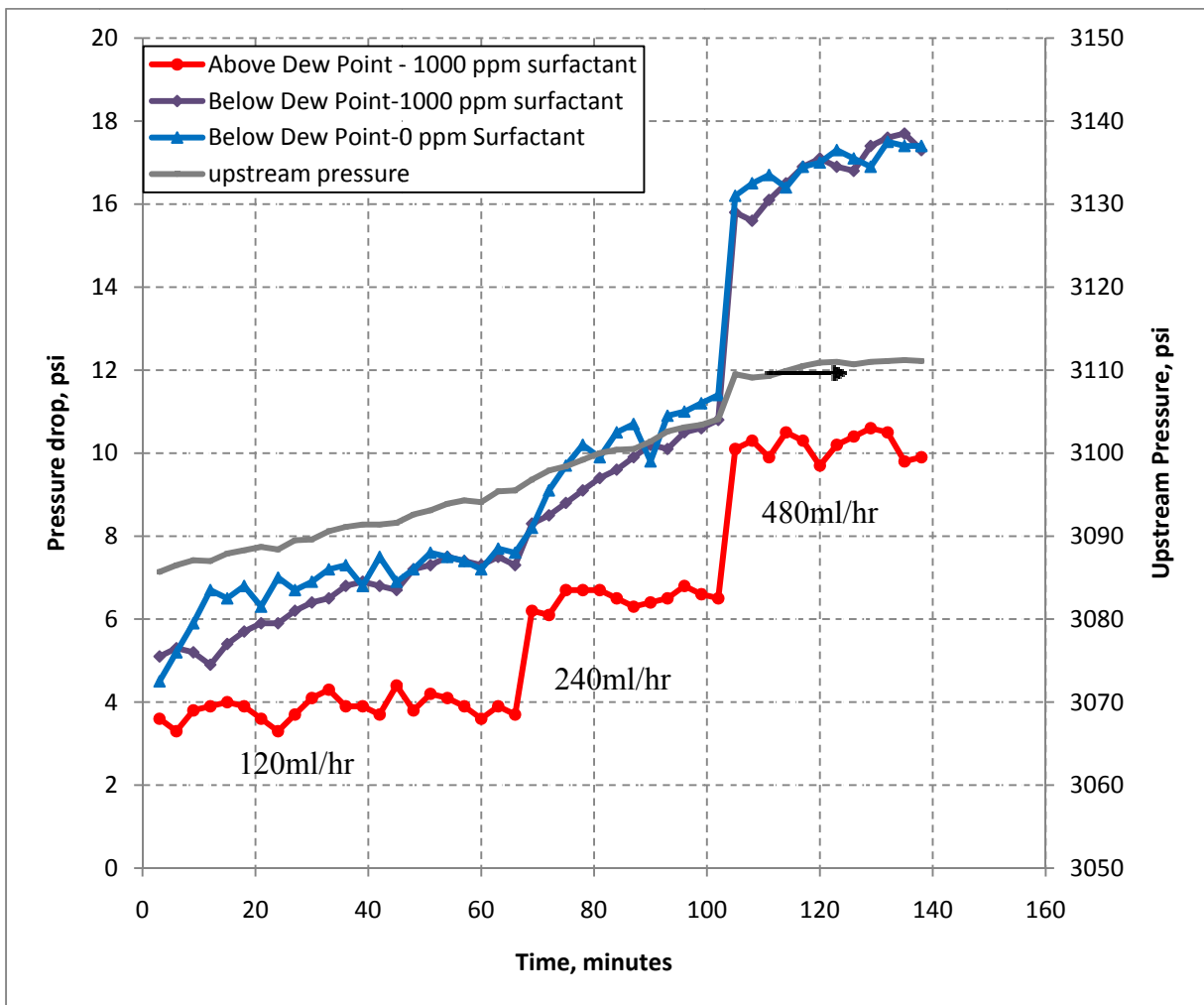


Figure 4.4 Pressure drop comparison between 1000 ppm & brine without surfactant

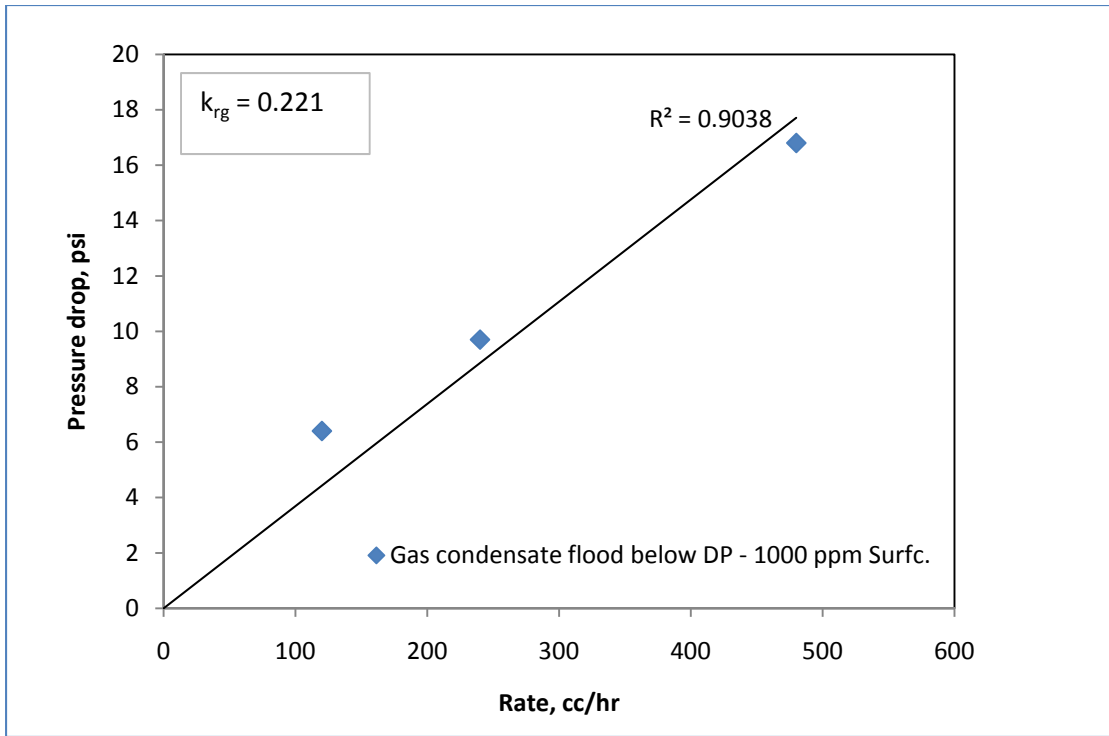


Figure 4.5 Relative permeability below dew Point – 1000 ppm surfactant case

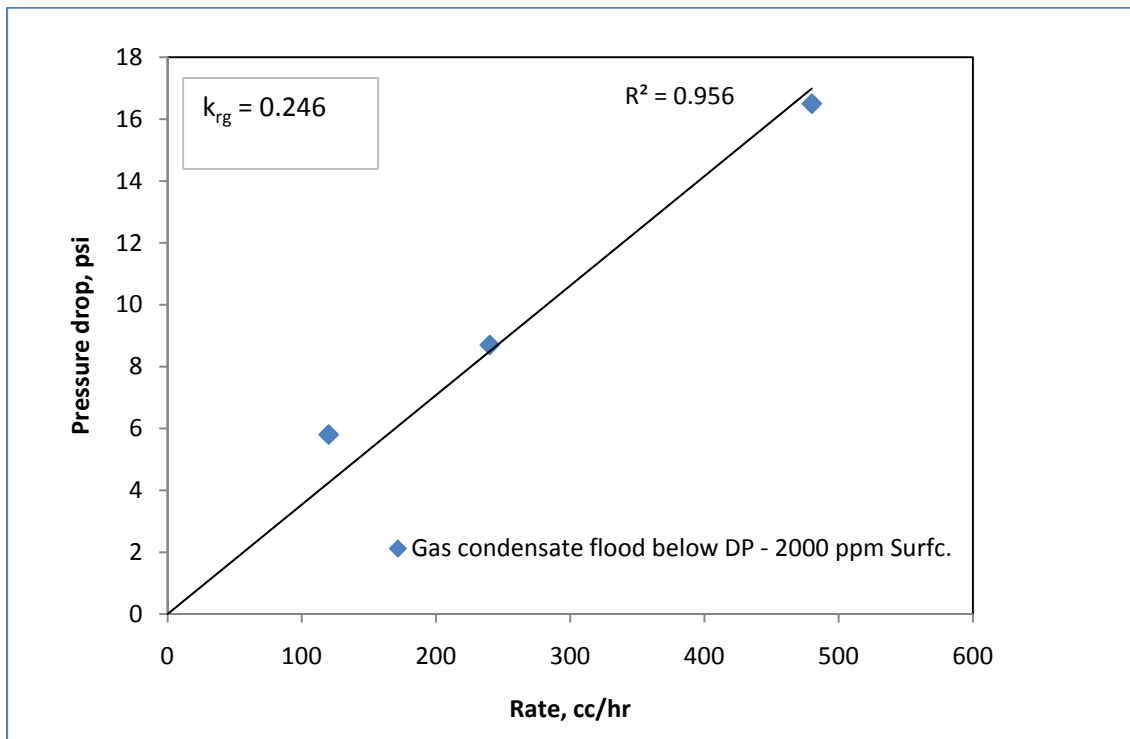


Figure 4.6 Relative permeability below dew Point – 2000 ppm surfactant case

4.3 Saturation with Brine Containing 2000 ppm Surfactant Concentration

Figure 4.6 shows the comparison of pressure drops above and below the dew point for the 2000 ppm surfactant case with that of the Brine without surfactant. Here, a relatively stronger effect to the presence of surfactant is observed even though the effect seems to taper off at the highest flow rate of 480 ml/hr. The gas relative permeability reduction is only 31.4% compared to 41.5% for the brine without surfactant case. In other words, substantial improvement in relative permeability of 17.2% is obtained for the 2000 ppm surfactant case over the brine without surfactant case.

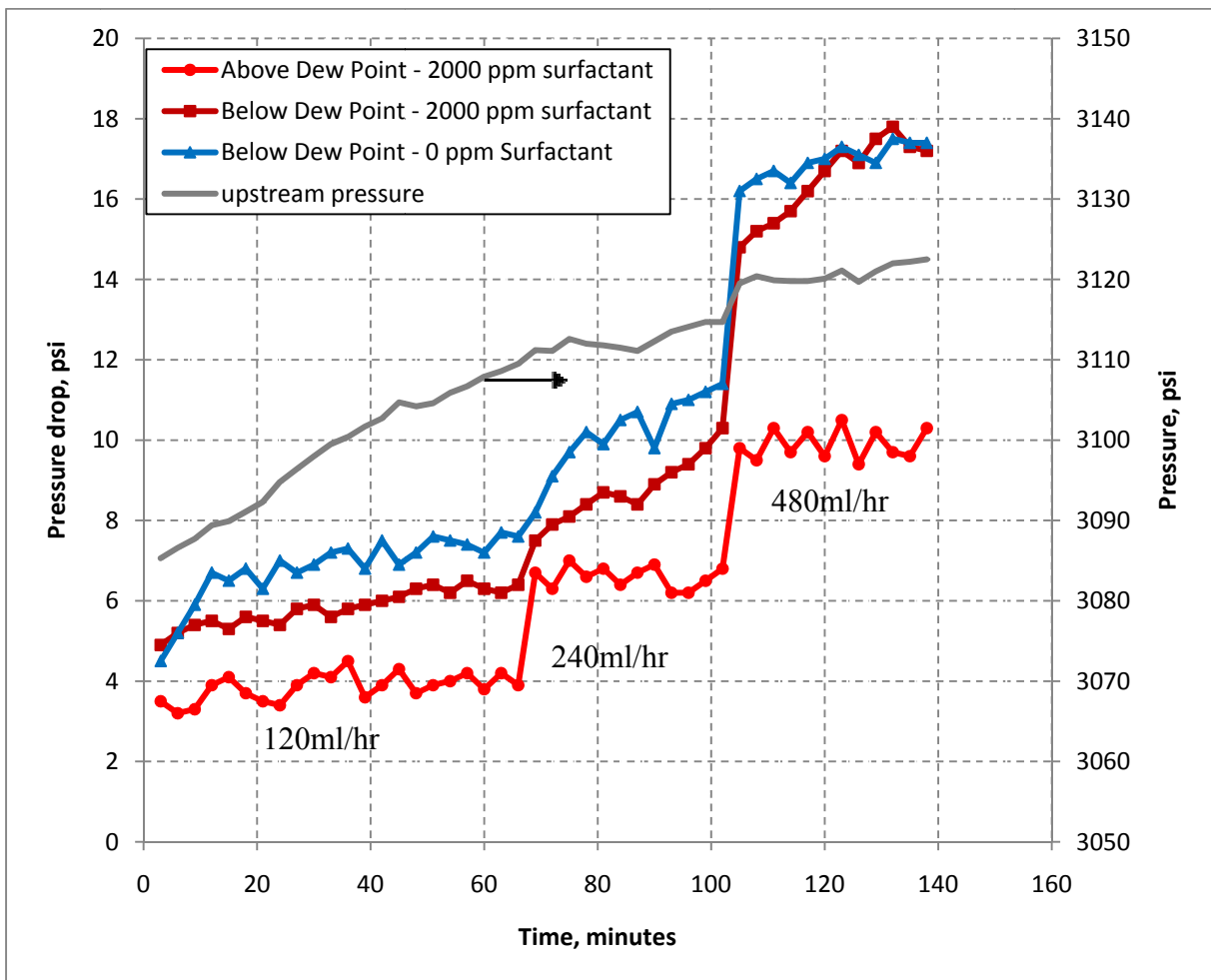


Figure 4.7 Pressure drop comparison between 2000 ppm & brine without surfactant

4.4 Saturation with Brine Containing 5000 ppm Surfactant Concentration

Figure 4.8 and 4.10 show the comparison of pressure drops above and below the dew point for the 5000 ppm surfactant case with that of brine without surfactant and 2000 ppm surfactant case respectively. There is no significant improvement over the 2000 ppm surfactant case in the pressure drop response for flow rates of 120ml/hr and 240 ml/hr but there is tangible effect for the flow rate of 480ml/hr. The gas relative permeability reduction is marginally low at 30.6% compared to 31.4% for the 2000 ppm surfactant case. The improvement in relative permeability is also slightly higher at 18.6% compared to 17.2% for the 2000 ppm surfactant case.

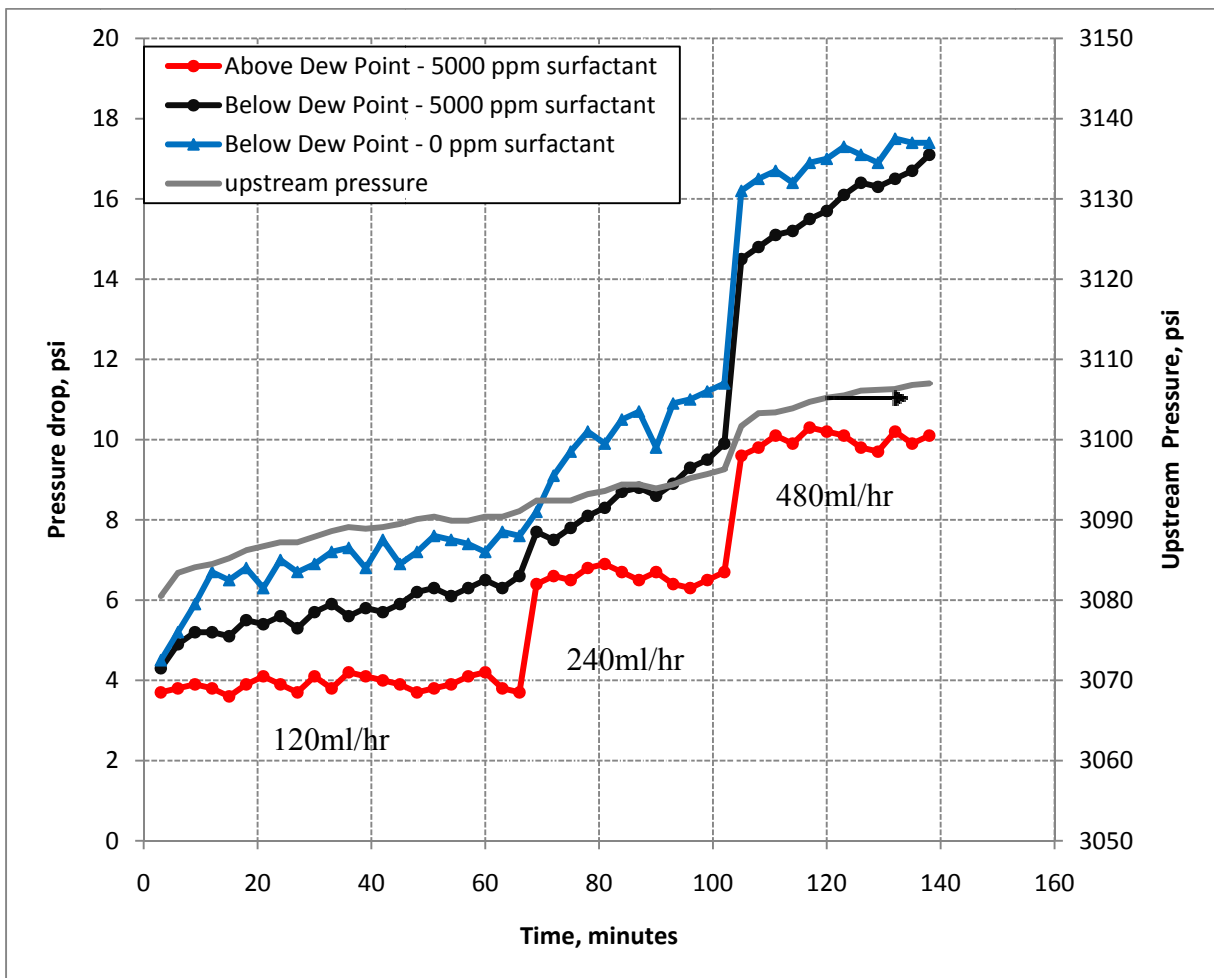


Figure 4.8 Pressure drop comparison between 5000 ppm & brine without surfactant

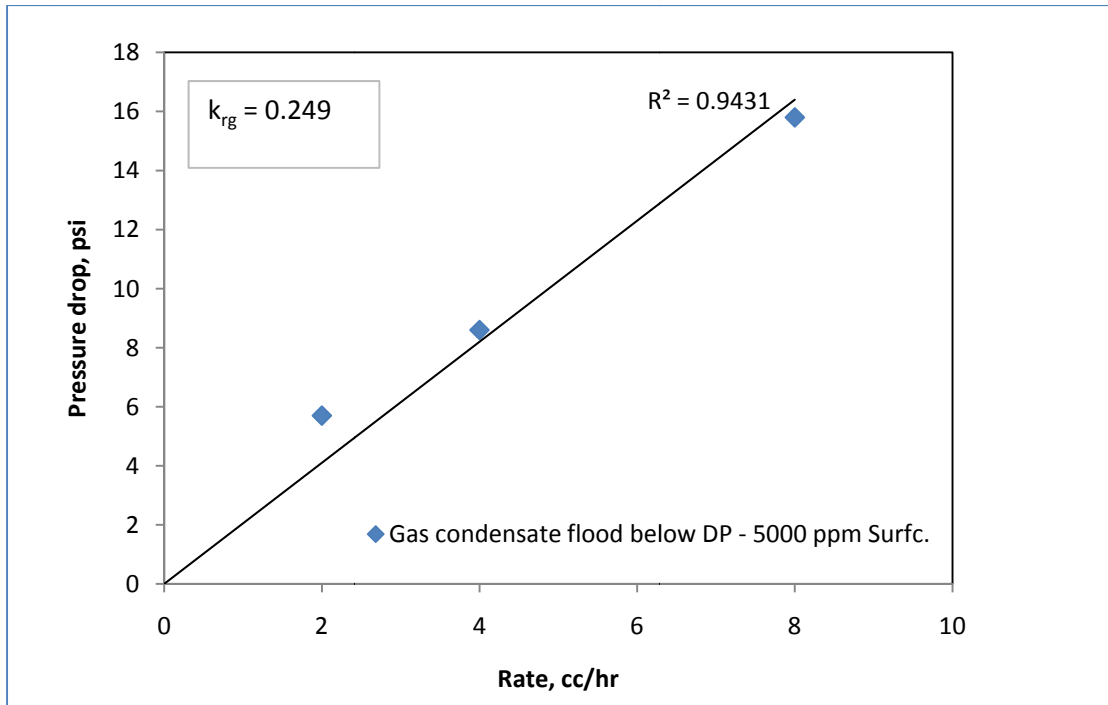


Figure 4.9 Relative permeability below dew Point – 5000 ppm surfactant case

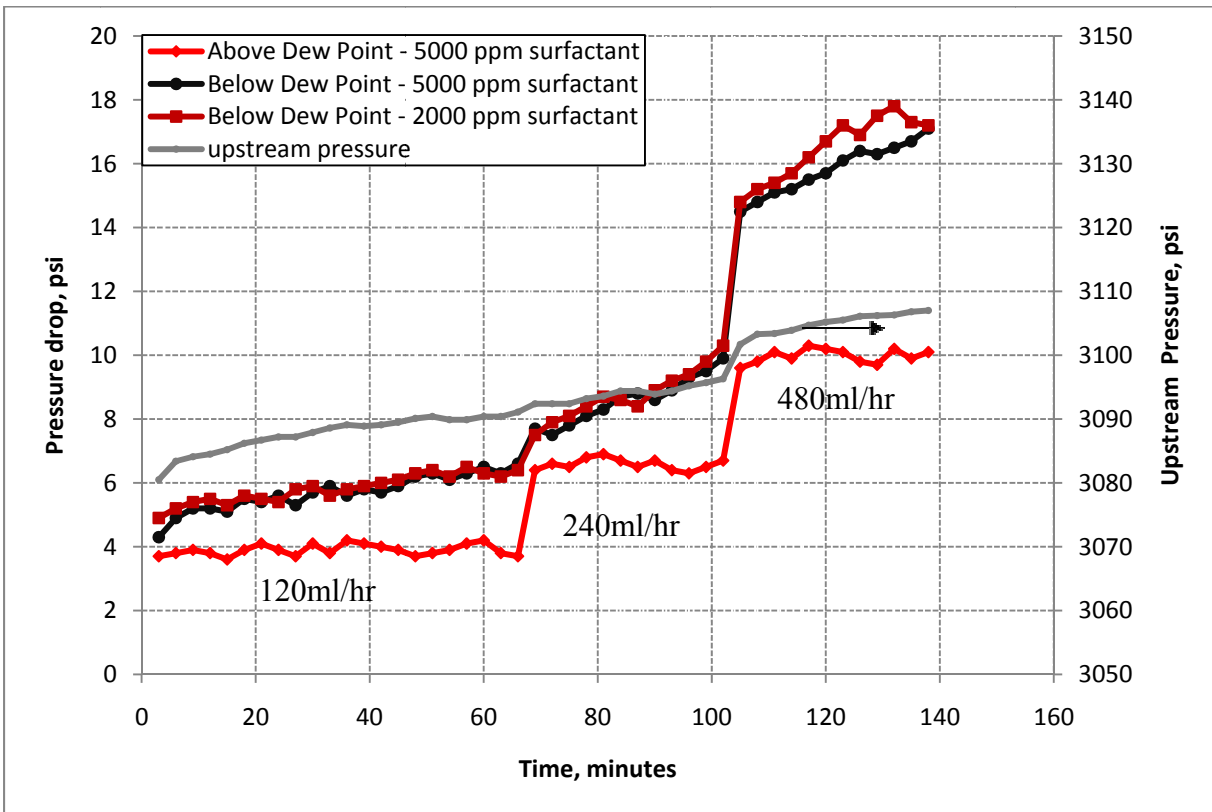


Figure 4.10 Pressure drop comparison between 5000 ppm and 2000 ppm surfactant

4.5 Comparative Analysis of Pressure Drops

Figure 4.11 shows the comparison of pressure drops for all the four cases put together. The closeness in the placement between graphs for 2000 ppm and 5000 ppm surfactant cases implies that there is not significant incremental effect with higher surfactant concentration above a surfactant concentration of 2000 ppm. This proximity between the 2000 ppm and 5000 ppm surfactant concentrations is pronounced till the flow rate of 240 ml/hr, showing its optimum range of flow conditions for this surfactant concentration.

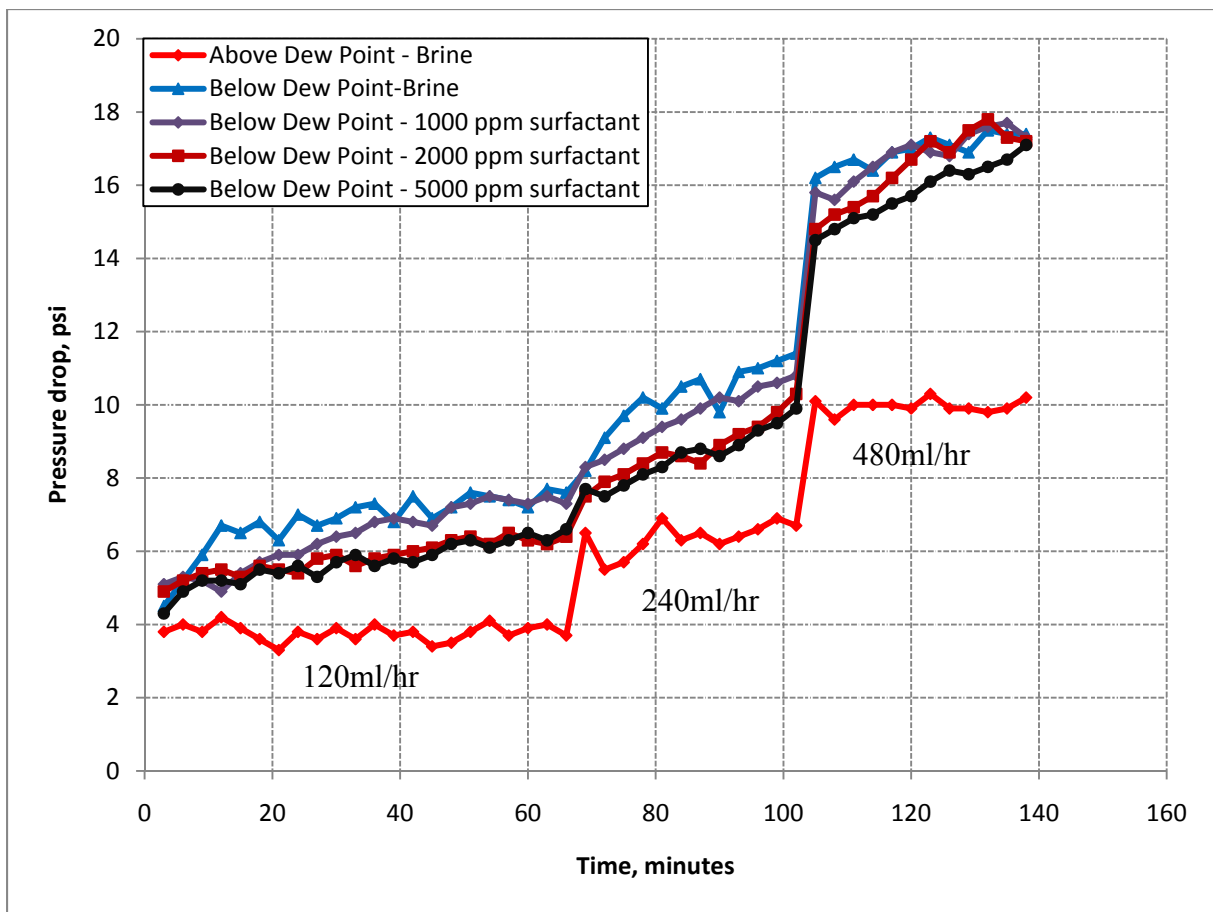


Figure 4.11 Pressure drop comparison for all four cases

The pressure drops are also plotted with respect to flow rate at different surfactant concentrations in Figure 4.12. There is visible decrease in pressure drop with respect to concentration at the various flow rates considered. There is maximum reduction in pressure drop for the 5000 ppm

surfactant case, depicted by its bottom most position on the graph. This plot thus illustrates the effectiveness of the surfactant in reducing pressure drop, thereby improving relative permeability of the retrograde gas at all flow rates.

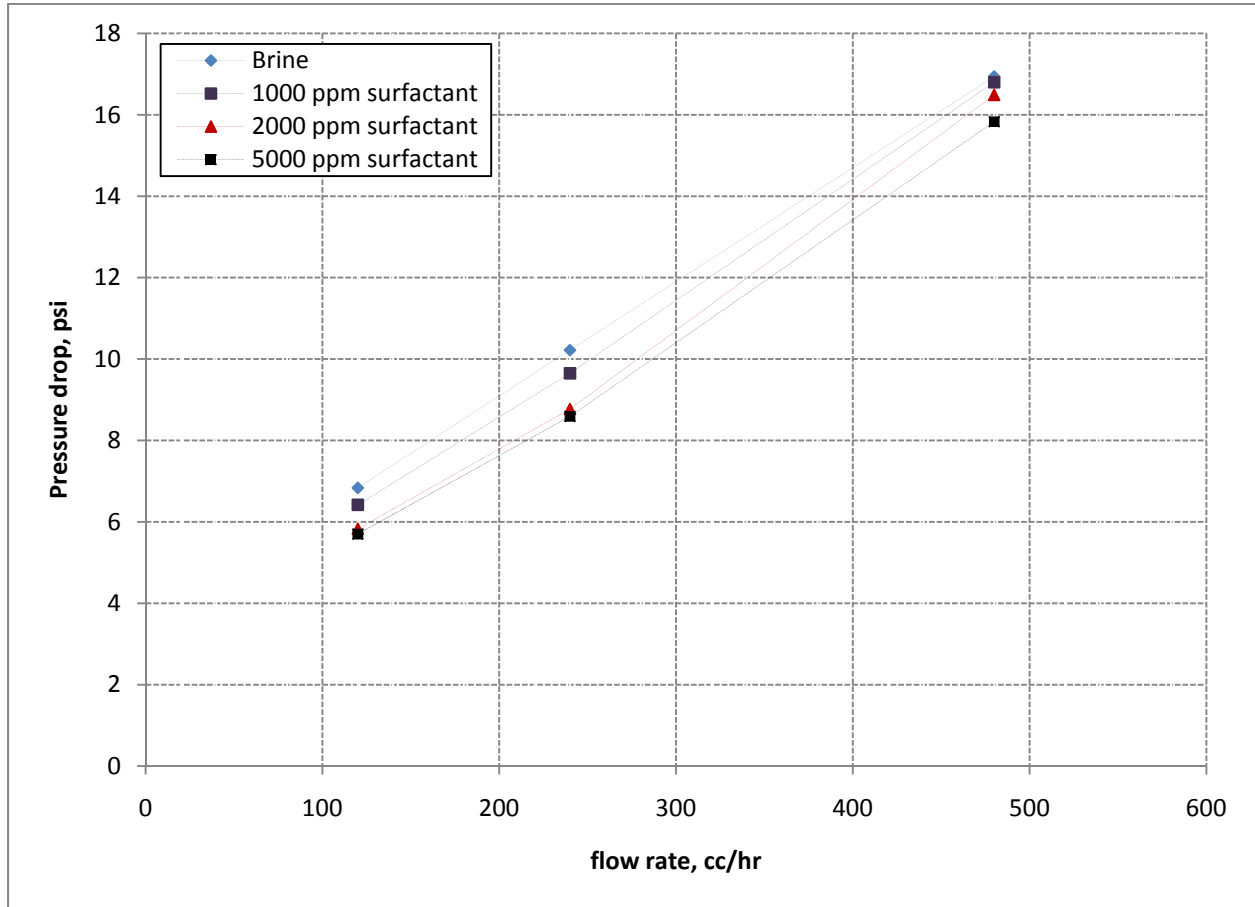


Figure 4.12 Effect of surfactant concentration on ΔP at various flow rates

Figure 4.13 shows the effect of surfactants on dimensional pressure drop. The percentage decrease in dimensional pressure drop is 6.1%, 14.7% and 16.6 % for the concentrations of 1000 ppm, 2000 ppm and 5000 ppm respectively, considering only the flow rate of 120ml/hr. Both 2000 ppm and 5000 ppm surfactant concentrations are able to affect considerable reduction in the dimensional pressure drop. Nevertheless, the incremental reduction in dimensional pressure drop for the 5000 ppm surfactant case over 2000 ppm surfactant concentration is not significant, hence 2000 ppm serves as the optimum concentration among others. In terms of economics,

2000 ppm surfactant is a better choice over 5000 ppm surfactant as surfactants are expensive chemicals.

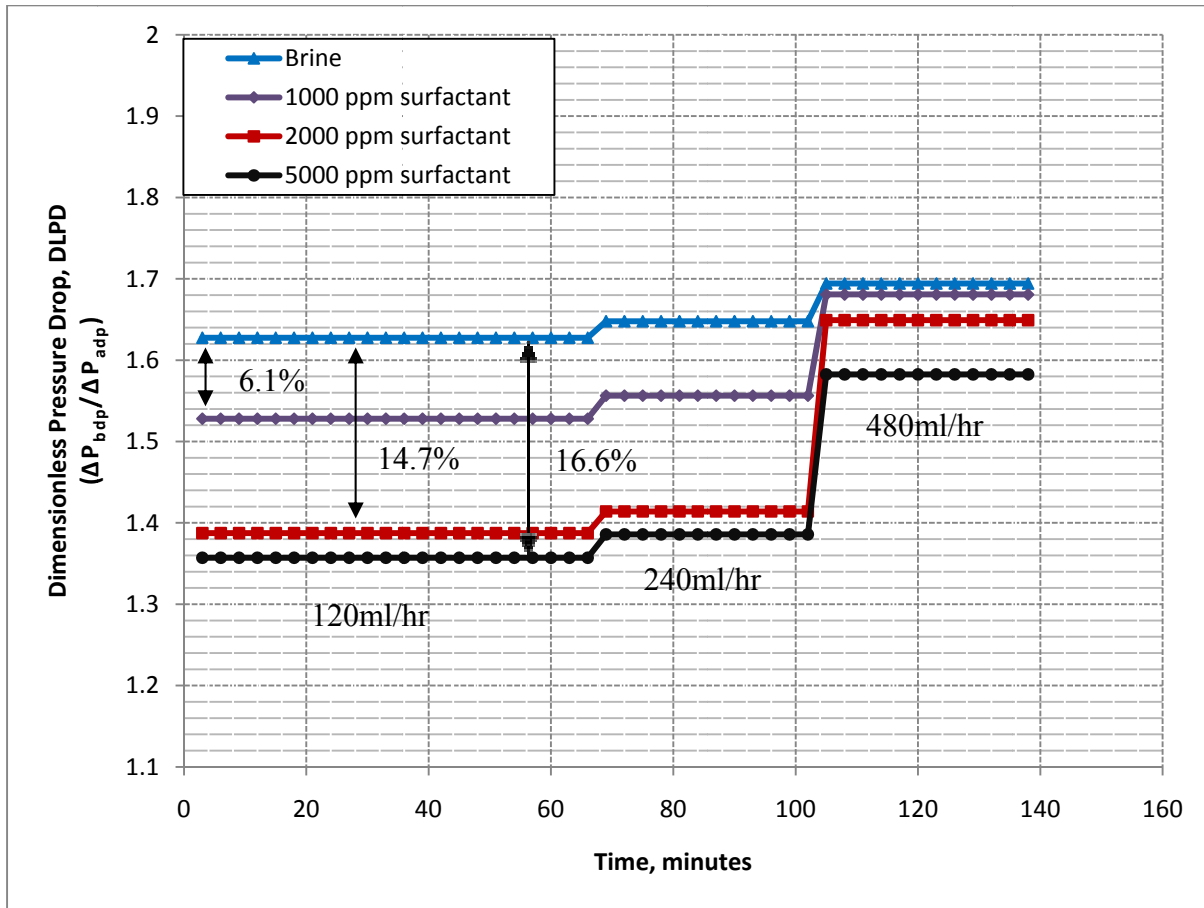


Figure 4.13 Effect of surfactant concentration on dimensionless ΔP (DLPD)

The marginal increment in the efficacy of the surfactant despite a significant increase in the concentration may be explained by the concept of critical micellar concentration (CMC). Critical micellar concentration is the threshold concentration below which the surfactants are composed only of monomers and the surface is under saturated. Adsorption on rock surface also is Langmuir type. At low concentrations, the orientation of surfactant molecule is such that the hydrophobic tail group is aligned with the surface. With the increase in the surfactant concentration gradually this alignment changes and surfactant molecules tend to take orthogonal orientations with respect to the surface causing wettability alteration⁹. Above CMC, the

surfactants have the tendency to aggregate or form conglomerates called micelles and from here on the monomer concentration remains relatively constant with increasing surfactant concentration as the surface saturation has been reached. Table 4.3 gives the summary of the important results obtained from the experiments.

Table 4.3 Summary of important results

Sl. No.	Parameter	Value
1	Dry gas relative permeability above dew point at S_{wi}	0.359
2	Gas relative permeability below dew point for the brine (base) case	0.210
3	Gas relative permeability below dew point for the 1000 ppm surfactant case	0.221
4	Gas relative permeability below dew point for the 2000 ppm surfactant case	0.246
5	Gas relative permeability below dew point for the 5000 ppm surfactant case	0.249
6	Gas relative permeability reduction for brine without surfactant	41.5%
7	Gas relative permeability reduction for the 1000 ppm surfactant case	38.5%
8	Gas relative permeability reduction for the 2000 ppm surfactant case	31.4%
9	Gas relative permeability reduction for the 5000 ppm surfactant case	30.6%
10	Improvement in gas rel. permeability of 1000 ppm surfactant over base case	5.2%
11	Improvement in gas rel. permeability of 2000 ppm surfactant over base case	17.2%
12	Improvement in gas rel. permeability of 5000 ppm surfactant over base case	18.6%

A rising trend in the pressure drop has been observed in the below-dew-point runs at all flow rates considered. This increasing trend in the pressure drop appears to be due to the increased liquid dropout occurring with time as the mixture undergoes retrograde condensation at pressures below the dew point. This is further substantiated by the absence of such a pressure drop increase

in the case of above-dew-point runs. The presence of surfactants does help in mitigating this increased dropout, as can be seen from Figure 4.12 where the pressure drop decreases with increasing surfactant concentration, but is not able to nullify it completely.

Alfoterra class of anionic surfactants that was used in our experiments was also reported to be a better agent at wettability alteration on calcite surfaces to intermediate wet compared to cationic surfactant by Seethepalli et al.⁴⁴.

It has also been observed through these flow experiments that higher concentration of surfactant is required than those expected from wettability and IFT measurements (Zheng et al.⁵⁴) as a result of inherent inefficiencies in the delivery and retention of the surfactant.

4.6 Economic Impact Evaluation

To evaluate the economic impact of the enhancement in relative permeability on a representative well producing retrograde gas, a typical gas composition have been assumed for the gas mixture as given in Table 4.4. Some typical parameters have also been assumed for the well as given in Table 4.5.

The rate equation has been solved using pseudo pressure integral method for various cases. Steady state solution of the diffusivity equation is used. The standard conditions assumed are $P_{sc}=14.7$ psia and $T_{sc}=60^{\circ}F$. An example calculation for “No blockage case” has been illustrated below.

Table 4.4 Typical gas composition for the well

Component	Mole %
CH ₄	97.75
CO ₂	2
N ₂	0.25

Table 4.5 Typical Parameters for the well

Parameter	Value	Units
k (Permeability)	10	mD
h (Pay thickness)	100	ft
T (Temperature)	300	⁰ F
r _e (External radius)	1000	ft
r _w (Wellbore radius)	0.25	ft
P _{r avg.} (Average reservoir pressure)	7000	psia
k _{rg} (No blockage)	0.359	-
k _{rg} (Before treatment)	0.21	-
k _{rg} (After treatment)	0.246	-
Natural Gas Price (Average)	4	\$/Mscf

Q_g , Mscf/day (Gas flow rate with No blockage):

$$\begin{aligned}
 [Q_g, \text{Mscf/day}]_{\text{No blockage}} &= \alpha_2 \times (kk_{rg}h/T)_{\text{No blockage}} \times \{P_p(P_{r \text{ avg.}}) - P_p(P_{wf})\} / \ln(r_e/r_w) \\
 &= 0.0007032 \times 1.19667 \times \{2073365523 - 1660219694\} / 8.29404964 \\
 &= 46,084.08 \text{ Mscf/day}
 \end{aligned}$$

The gas flow rates obtained for the various cases are given in the Table 4.6.

Table 4.6 Gas flow rate for various cases

Cases	Gas flow Rate, Mscf/day
No blockage	46,084.08
Blockage (Before treatment)	26,957.26
Blockage (After treatment)	31,578.50

So, Incremental gas production on treatment is = (31,578.50 – 26,957.26) Mscf/day

$$= 4,621.24 \text{ Mscf/day}$$

Incremental revenue per day = 4,621.24 Mscf/day X \$4/Mscf

$$= \$18,484.98/\text{day}$$

Incremental revenue per year = \$18,484.98/day X 365 days

$$= \underline{\underline{\$6,747,016.92/\text{year}}}$$

The above calculations for incremental revenue have been made for a single well bottom hole pressure of 6000 psi. However, well bottom hole pressure can take any values based on operating requirements. Figure 4.14 shows the incremental revenue per year with respect to well bottom hole pressures upto absolute open flow pressure.

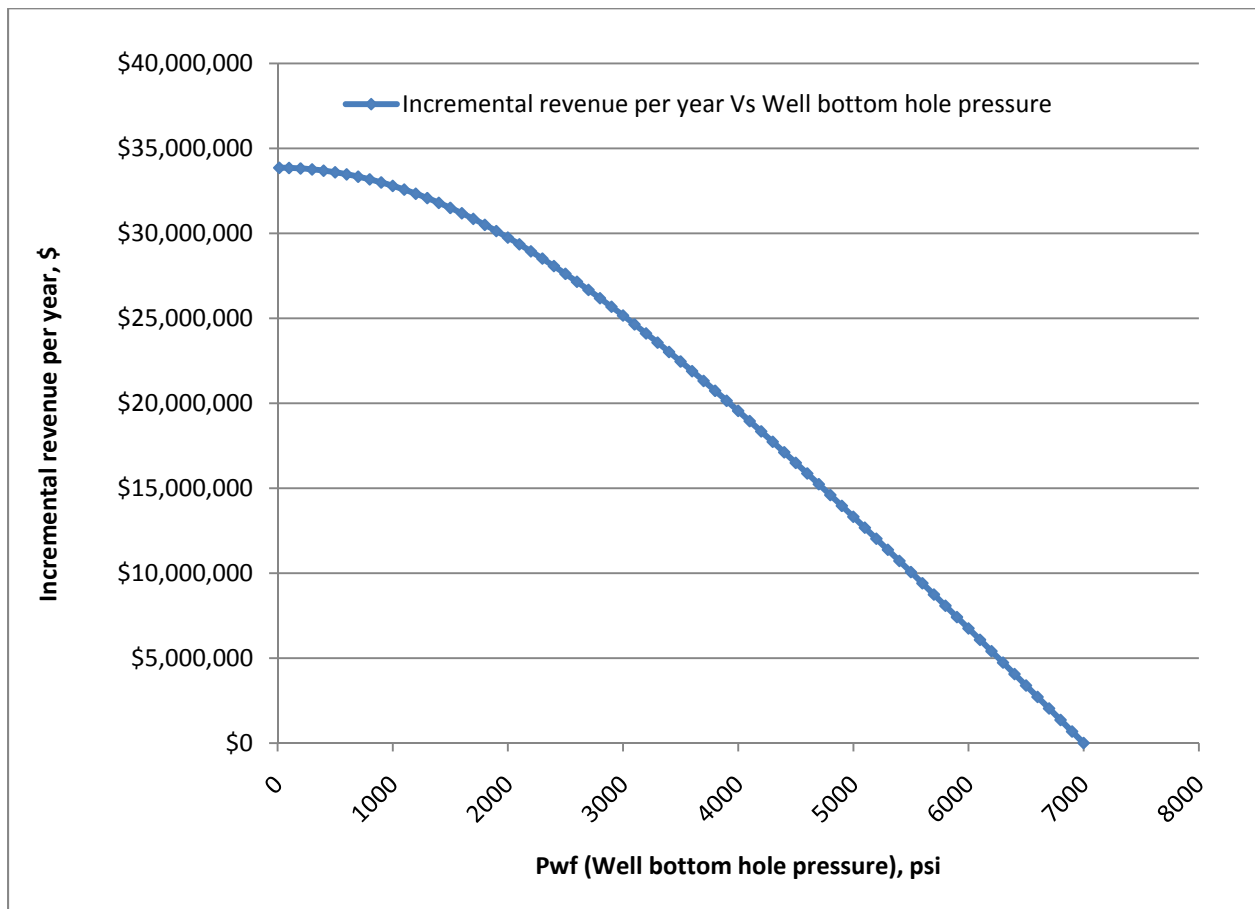


Figure 4.14 Incremental revenue per year Vs well bottom hole pressure

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

5.1 Summary and Conclusions

Core flood experiments incorporating in-situ retrograde condensation were carried out to quantify the effect of surfactants on the flow behavior of gas condensates. Two types of mechanisms by which surfactants impact the flow behavior of the gas condensates: spreading coefficient modification and wettability alteration. These mechanisms act simultaneously to affect the primary task of condensate blockage remediation. Series of experiments with increasing concentration of surfactants were conducted both above and below the dew point and the salient results obtained have been summarized below.

- A retrograde gas mixture was designed capable of undergoing retrograde condensation at ambient temperature.
- An experimental apparatus was built in house with the capability of creating in-situ retrograde condensation.
- Successful condensate removal was observed with anionic surfactant Alfoterra® 123-4S, provided by Sasol Surfactants, when condensate dropped out from the retrograde gas mixture with the lowering of pressure below the dew point pressure. A surfactant concentration of 2000 ppm appeared to be the optimum under the flowing conditions for the removal of condensates.
- The effect of the surfactant was observed to be a non linear function of its concentration. This is attributed in part mainly to the plateauing effect in their efficacy above the critical micellar concentration (CMC) values and to a lesser extent on the suitability of the particular wettability state of the rock surface to the flow conditions and also to mechanisms of surfactant adsorption and retention.

5.2 Recommendations for Future Work

- Mode of delivery of surfactants in a field scale setting need to be devised so as to maximize their benefits with minimum of wastage.
- Physics of surfactant retention at fluid/fluid and rock/fluid interfaces need to be better understood vis-à-vis different rock types and reservoir conditions through wettability, micro-model, spectroscopy studies etc. so as to be able to screen the right type of surfactant to suit specific rock types and conditions for enhancing their performance.
- Longer tests need to be conducted with a wide range of flowing conditions to determine the effect of the durability of surfactant treatment and its applicability.
- Pilot scale studies of the treatment need to be conducted for assessing its application on field scale.
- Effect of surfactants on flow behavior of gas condensates in limestone reservoir rocks need to be characterized.
- The temperature and salinity effects on flow behavior induced by surfactant needs be studied.

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