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Phase Behavior Study of Hydrocarbon-Water-Alcohol Mixtures

by

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Phase Behavior Study of Hydrocarbon-Water-Alcohol Mixtures

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Dedication

To Humanity
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Abstract

Phase Behavior Study of Hydrocarbon-water-Alcohol Mixtures

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Experiments were performed to study the phase behavior of gas condensate hydrocarbons at reservoir conditions. Constant composition measurements were done on synthetic gas condensate mixtures and the results were used to regress the Peng-Robinson equation-of-state with the temperature-dependent Peneloux volume corrections and classical van der Waals mixing rule (PR78 Peneloux (T)).

Experiments were performed to study the effect of water and methanol on the phase behavior of gas condensate hydrocarbons. Effects of various factors including temperature, pressure and the molar concentrations of water and methanol on the phase behavior of hydrocarbon-water-methanol mixtures were studied. Addition of methanol increased the liquid volume fraction and the dew point pressure when added to the hydrocarbon mixture. However, for hydrocarbon-water-methanol mixtures the aqueous
phase volume fraction increased while the dew point pressure decreased with increasing mole fraction of methanol. PR78 Peneloux (T) equation of state was used to model hydrocarbon-water-methanol mixtures. The EOS was regressed to match the experimental data by tuning the binary interaction coefficients between components and their volume shift parameters. The mixtures were also modeled using Peng-Robinson equation of state with temperature-dependent Peneloux volume shift correction factors and Huron-Vidal mixing rules (PR78 Peneloux (T)-HV). The calculations from both the EOS models agree quantitatively with the experimental results. The binary interaction parameters were found to be temperature dependent. The binary interaction parameters and the temperature-dependent volume shift parameters are the key parameters to model these complex mixtures using any EOS model. The multiphase flash capability of PVTSim software by Calsep Inc. was used to calculate the phase diagrams since the phase behavior is sometimes three-phase liquid-liquid-vapor under the experimental conditions.

Phase behavior experiments were also performed on hydrocarbon-water-isopropanol (IPA) mixtures to investigate the effects of isopropanol on the phase behavior of gas condensate hydrocarbons. The results show that IPA decreases the aqueous phase volume fraction and increases the liquid hydrocarbon phase volume fractions when compared to the analogous hydrocarbon-water-methanol mixtures. Finally, the effect of fluorosurfactants FC4432 and S10 on the phase behavior of gas condensate hydrocarbon-water-methanol mixtures was studied experimentally.
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Chapter 1: Introduction

1.1 Introduction

Natural gas has become an important source of global energy. At present, natural gas provides approximately a quarter (25%) of the world's energy and its share is increasing significantly. Natural gas has also become the most desirable source of energy from the standpoint of global environmental problems. A rapid increase in worldwide demand of natural gas has resulted in significant growth of international gas trade and encouraged long-term contracts for its sales. Hence, it becomes important to accurately predict the production performances of these reservoirs.

Many of the natural gas reservoirs have reservoir conditions, which result in retrograde condensation due to pressure decreases during the production of gas. During depletion of gas condensate reservoirs as the pressure falls below the dew point pressure of the reservoir gas, condensate drops out of the gas phase and forms a condensate bank near the well bore. Very high flow rates in the near well bore region result in non-Darcy or inertial pressure drop in the region. These near wellbore effects (condensate accumulation and non-Darcy flow) reduce the gas productivity significantly.

Most gas condensate reservoirs are high pressure and high temperature reservoirs. These extreme conditions make the fluids thermodynamically complex. Some of the gas condensate reservoirs are near critical. This makes the phase behavior of such fluids very complex and difficult to predict using conventional methods.

One of the most important steps in better performance prediction of gas condensate reservoirs is the correct phase behavior modeling of gas condensate fluids. In most cases, gas condensate fluids have an underlying aquifer, which results in three phases in the reservoir. The presence of water or alcohols (added to treat condensate
blocks) or both makes the phase behavior of gas condensate hydrocarbons more complex. Such mixtures cannot be modeled using conventional equation of state models and require modified equation of state parameters for correct phase behavior modeling.

**1.2 Research Objectives**

The objective of this research project is to experimentally study the phase behavior of gas condensate hydrocarbons-water-alcohol mixtures at reservoir conditions and model them using commonly used cubic equations of state. The main objectives can be summarized as:

- Experimental phase behavior study of the pure hydrocarbon mixtures over a wide range of temperatures.
- Experimentally study the effect of water and alcohols on the phase behavior of hydrocarbons.
- Phase behavior modeling of pure hydrocarbon mixtures and hydrocarbon-water-alcohol mixtures using Peng-Robinson equation of state with Peneloux volume correction.
- To compare the equation of state phase behavior calculations for hydrocarbon-water-alcohol mixtures using classical and Huron-Vidal mixing rules.
- To experimentally study the effect of fluorosurfactants FC-4432 and S10 on the phase behavior of hydrocarbon-water-methanol mixtures.

The phase behavior results of hydrocarbon-water-methanol mixtures is important to interpret the results of the successful methanol treatments in removing condensate blocks, shown by Walker *et al.* (2000) and Al-Anazi (2003). The phase behavior modeling is also important to get the equation of state parameters for accurate phase
behavior predictions for these mixtures. This is essential for better production performance predictions for gas condensate reservoirs using compositional simulators.

1.3 REVIEW OF CHAPTERS

Chapter 2 is a literature review on the phase behavior aspects of gas condensate reservoirs. The chapter reviews the studies related to productivity decline in gas condensate reservoirs, coreflood studies done to measure gas-condensate relative permeabilities in the lab, treatments proposed to remove condensate blocks, performance predictions from gas condensate wells using compositional simulators and studies on phase behavior of gas condensate fluids.

Chapter 3 describes the experimental apparatus and procedure used for the phase behavior studies. In the first section, the high pressure-high temperature apparatus used for the experiments are described. This is followed by a description of the experimental setup, the procedures of gas mixture preparation and constant composition expansion experiments. In later sections, the PVT software and the equation of state calculations used for the phase behavior calculations are described.

Chapter 4 presents results of the phase behavior studies of gas condensate hydrocarbon mixtures with water and alcohols. First a phase behavior study of hydrocarbon mixtures is presented. This is followed by phase behavior studies of gas condensate-methanol and hydrocarbon-water-methanol mixtures. Later the effect of isopropanol on the phase behavior of hydrocarbon-water mixtures is presented. Finally, the effect of fluorosurfactants on the phase behavior of hydrocarbon-water-methanol mixture is shown.

Chapter 5 summarizes the results, presents conclusions and suggestions for future work.
Chapter 2: Literature Review

2.1 Productivity Decline in Gas Condensate Reservoirs:

In gas condensate reservoirs, when the bottomhole pressure in flowing wells falls below the dew point pressure of the fluid, a liquid hydrocarbon phase called condensate is formed. The condensed liquid is trapped by the capillary forces or is retained in the rock as a result of low liquid permeability. Condensate formation results in build up of a liquid phase around the wellbore; leading to a decrease in the effective permeability to gas. The liquid continues to accumulate, occupying portions of the rock pores that otherwise would be available for gas flow, and thus impeding gas flow, until a critical liquid saturation is reached that is similar to the value for residual oil saturation that would form in the same rock under the same flow conditions. Once the critical liquid saturation is exceeded, both the condensate and gas flow towards the wellbore, but condensate continues to form and accumulate until a steady state saturation is reached that is somewhat higher than the critical condensate saturation. This phenomenon is called "Condensate Banking." Condensate banking can reduce the well productivity significantly, in several instances by a factor of 2 to 4.

Forecasting production from gas condensate reservoirs is complex, due to the production of gas, condensate, and in many cases, water or reservoir brine. The decline in well productivity due to liquid build up around the near wellbore region depends on several factors - fluid phase behavior, basic rock and fluid properties, wettability, gravitational forces, flow characterized by interfacial and viscous forces, non- Darcy and
non-equilibrium effects, type of the well (vertically fractured, horizontal etc) and mixing with the gas in the region where condensate has already accumulated.

Afidick et al. (1994) studied the decline in productivity of Arun gas condensate reservoir due to condensate accumulation. Experimental PVT analysis of the reservoir fluid showed that the reservoir fluid was a lean gas condensate with maximum liquid dropout of 1.1%. The decline in the productivity of the wells by a factor of around 2 as the reservoir pressure fell below the dewpoint pressure was attributed to accumulation of condensate around the wellbore. The accumulation of condensate around the wellbore was confirmed by well tests and the analysis done on the reservoir cores.

Barnum et al. (1995) found that production loss is severe for low productivity reservoirs i.e. those with a kh less than 1000 md-ft. They reported that the critical condensate saturation ranged from 10-30% and can decrease the productivity by a factor up to five due to condensate accumulation near the wellbore.

Engineer (1985) studied Cal Canal Field in California, which produced a very rich gas condensate fluid and had a very high water saturation of 59%. Due to high condensate and water saturation in the near wellbore region, the total gas recovery expected form the field is as low as 10%. Boom et al. (1996) showed that even for lean fluids with low condensate dropout, high condensate saturations could build up as many pore volumes of gas pass through the near wellbore region.

2.2 Relative Permeability Studies:

Because the most important and complex phenomena associated with condensate banking and productivity reduction is relative permeability, there have been many investigations of gas-condensate relative permeability and a few of these are reviewed below.
Ham et al. (1967) conducted one of the earliest laboratory measurements done on gas condensate fluids. The authors used nitrogen and separator liquid from a reservoir condensate for their study. They evaluated the characteristic effect of several parameters including condensate saturation, pressure, apparent velocity, flowing liquid-vapor volume ratio, fluid composition and core type on the mobility of gas. The authors showed that relative mobility and liquid-vapor volume ratio relationships are dependent on pressure, saturation and, to a lesser extent, on velocity. The authors also showed that the critical condensate saturation is dependent on pressure and velocity.

Bourbiaux et al. (1994) and Kalaydjian et al. (1996) designed an experimental procedure to measure the critical condensate saturation (Scc) and the relative permeabilities of gas and condensate. The authors also measured on-stream condensate dropout and local condensate saturation using a gamma ray attenuation technique with a specific method of calibration. The authors found that Scc is related to initial water saturation (Swi), with the total critical liquid saturation remaining constant around 26% of the pore volume for the cases they studied.

Henderson et al. (1998) measured steady state relative permeabilities for gas condensate fluids over a wide range of CGR (condensate to gas ratio), IFT (interfacial tension) and velocities. The authors found that relative permeabilities of both gas and condensate phases are rate sensitive and increase with velocity. The relative permeabilities were also sensitive to the IFT and increased with lowering of IFT.

Chen et al. (1999) performed relative permeability measurements for two North Sea gas condensate fluids to investigate the effects of rock and fluid characteristics on critical condensate saturation and gas and condensate relative permeability. The authors used recombined fluids from two North Sea gas condensate reservoirs and 29' composite cores for their study. Their results showed that critical condensate saturation and relative
permeability are sensitive to flow rate and interfacial tension. The authors also showed
the condensate relative permeability curve exhibits an unusual convex curvature when
plotted against condensate saturation. The authors suggest that high interfacial tension
cause the decrease in condensate relative permeability with increasing condensate
saturations.

Saevareid et al. (1999) conducted steady state coreflood experiments for gas
condensate fluids and measured gas and condensate relative permeability as a function of
gas-oil interfacial tension and velocity. The authors showed significant improvement in
gas and condensate relative permeability with capillary number.

Mott et al. (2000) and Cable et al. (2003) conducted steady state coreflood
experiments for gas condensate fluids to examine the effect of capillary number on
relative permeability and distinguish the effect of high capillary number and inertial
effects on relative permeabilities at high flow rates. The authors concluded that at fixed
IFT, gas relative permeability increases with velocity and at a fixed capillary number, gas
relative permeability decreases with velocity due to inertial flow. Cable et al. (2003) also
did X-ray in-situ condensate saturation measurements at steady state conditions. Their
results showed that condensate saturation increases with higher capillary number at a
fixed value of $k_{rg}/k_{ro}$ and therefore the authors concluded that improved gas relative
permeability at high capillary number is not due to lower condensate saturation. This
result is in contradiction with the general perception that condensate saturation decreases
at higher capillary number.

Du et al. (2000), Walker et al. (2000) and Al-Anazi et al. (2003) showed from
their coreflood experiments that condensate dropout reduced the gas relative permeability
by an order of magnitude and the reduction is even more severe in presence of high water
saturation. The authors also showed that the decline in normalized PI (ratio of PI during
two phase flow to PI during single phase flow i.e. ratio of damaged PI to original PI) is almost the same for both high and low permeability rocks. Al-Anazi (2003) also showed that non-equilibrium mass transfer phenomenon occurred in the cores at high flow rates and required more pore volumes of injected fluid to reach steady state than if local equilibrium existed in the cores.

Ayyalasomayajula et al. (2003) conducted steady state coreflood experiments for gas condensate fluids and measured gas and oil relative permeability as a function of capillary number for several different reservoir rocks and for a wide range of \( k_{rg}/k_{ro} \) values. The authors showed significant improvement in gas relative permeability with capillary number for all the rock types.

The relative permeability measurements for gas condensate fluids done by the various authors have been analyzed by expressing gas and condensate relative permeability as a function of \( k_{rg}/k_{ro} \) and capillary number. Figures 2.1 and 2.2 show gas relative permeability reported by the various authors as a function of capillary number at \( k_{rg}/k_{ro}=1 \) and \( k_{rg}/k_{ro}=10 \) respectively. The data reported by all authors show an increase in gas relative permeability with capillary number, however the increase with capillary number is not consistent. Figure 2.3 shows the gas relative permeability reported by various authors expressed a function of \( k_{rg}/k_{ro} \) for a range of capillary numbers. Again the data reported by various authors show an increase in gas relative permeability with \( k_{rg}/k_{ro} \) ratio. The figures also show the comparison of the measured data with the gas relative permeability calculated using capillary number dependent relative permeability model by Pope et al. (2000). The results show that most of the measured data are scattered around the gas relative permeability curve calculated from the model, however some measured gas relative permeability data are off from the calculations, which is probably because of the differences in rock type and initial water saturations.
2.3 METHODS TO TREAT CONDENSATE BLOCKAGE:

Several methods have been proposed and investigated to treat damage caused by condensate accumulation. The most common approach to treat damage caused by condensate blocking are either to change the phase behavior of the gas condensate fluid or to reduce the pressure drawdown and maintain pressure above the dew point pressure.

Abel et al. (1970) described the two schemes of gas cycling: full pressure maintenance and partial pressure maintenance. In full pressure maintenance process, gas is continuously injected into the reservoir at the same time gas condensate is produced from the reservoir in an attempt to prevent reservoir pressure from falling below the dew point pressure. Whereas, in the partial pressure maintenance approach, gas is injected into the reservoir after primary depletion below the dewpoint, in an attempt to arrest or slow further pressure decline and revaporize or miscibly displace the condensate.

Processes that take place when injected gas contacts condensate liquid include:

a. Displacement of reservoir fluid by the injected gas

b. Re-vaporization of components because of mass transfer

c. Change in PVT behavior of reservoir fluid upon contact with the injected gas

Kossak et al. (1986) did simulations to study the performance of slug injection of methane followed by nitrogen. They studied the effect of slug injection in a homogeneous and heterogeneous layered reservoir with both isotropy and anisotropy. Their results show that the heterogeneities allow the nitrogen to mix with condensate when the methane slug is small but the incremental recovery with methane slug over nitrogen injection is large enough to pay off the cost of methane.

Sanger and Hagoort (1992) investigated the efficiency of nitrogen to evaporate gas condensate compared to methane. They found that methane can evaporate more condensate than nitrogen. The authors reported that the evaporation capacity of methane
is more that 20 times higher than that of nitrogen. The disadvantage of injecting nitrogen is that the dewpoint of the mixture is higher than the reservoir gas and thus leads to in-situ condensate drop out due to mixing with gas condensate in reservoir.

Ahmed et al. (1998) studied the effectiveness of lean gas, N₂, and CO₂ Huff ‘n’ Puff injection technique in removing the liquid accumulated in and around the wellbore. Huff ‘n’ Puff injection techniques use the same well alternatively as producer and injector. The authors concluded that pure CO₂ is the most effective gas in reducing the liquid dropout as compared to others when injected at the same pressure. The authors also show that the huff ‘n’ puff injection of gases is most effective when initiated before the maximum liquid dropout (from CVD) is reached. An insufficient amount of gas injection could increase the liquid dropout.

Luo et al. (2000) conducted experiments on an actual rich gas condensate fluid to investigate condensate recovery, based on the two pressure maintenance strategies mentioned above, to quantitatively determine the revaporization efficiency of retrograde condensate by lean gas injection. Their analysis of the produced condensate phase shows that a greater percentage of the heavier components are vaporized and recovered when gas is injected above the saturation pressure compared to when gas is injected below the saturation pressure. Their results also show that cumulative condensate recovery is higher when injection is done above the saturation pressure. The authors also observed that during gas injection at the reservoir pressure, the mass transfer between the dry-gas injected and the original gas condensate leads to a rise in dew point pressure and earlier retrograde condensation, which may reduce the condensate recovery to some extent.

Jamaluddin et al. (2001) did PVT experiments to study the effect of CO₂ and propane on the phase behavior of the reservoir gas condensate fluid. They found that CO₂ increases the dewpoint of the mixture but reduces the total liquid dropout below the
dewpoint whereas propane reduces the dewpoint as well as the total liquid dropout. The authors suggest Huff ‘n’ Puff injection of propane would efficiently reduce the damage due to condensate blocking.

Marokane et al. (2002) studied the injection of produced gas to remove the condensate bank for lean and rich gas condensate fluids. The authors found that to achieve maximum recovery for a lean gas condensate, produced gas should be injected after the average reservoir pressure around a producing well falls below the maximum liquid dropout pressure. For rich gas condensate, gas injection is more efficient when the produced gas is injected at a pressure greater than the maximum liquid dropout pressure.

Al-Anazi et al. (2004) experimentally studied the revaporization of condensate in cores by methane. The authors showed that methane flooding revaporizes condensate and restores the gas permeability to single-phase flow value. Revaporization of condensate was controlled by the partitioning of the hydrocarbon components into the flowing gas phase when the injection was done below the minimum miscibility pressure (MMP). Increase in injection pressure and rate expedited the revaporization of condensate.

Hoier et al. (2004) studied miscible gas injection for partial pressure maintenance in an under-saturated oil (Smorbukk South Field) exhibiting compositional variation. The authors' generated MMP (minimum miscibility pressure) gradient for a given injected gas, from the compositional, reservoir pressure and saturation pressure gradients. The authors concluded that once the injected gas develops miscibility at the injection point, the developed miscible front will first-contact miscibly displace the downstream fluid, independent of whether the downstream fluid is miscible or immiscible with the injected gas.

Henderson et al. (1991) performed coreflood experiments to study the effect of water injection on gas condensate recovery, above and below the dew point. They found
that residual hydrocarbon saturation after waterflooding depends on the prevailing IFT between the gas and condensate. The authors also showed that gas and condensate displacement by water is complex and cannot be represented by data from water-oil and water-gas displacements and requires special three-phase relative permeability measurements to describe waterflooding and subsequent depressurization.

Fishlock et al. (1996) studied the performance of water injection for lean and rich gas condensate fluid systems. They found that hydrocarbon recoveries are higher for leaner fluids than richer fluids because a higher proportion of oil is in the gas phase at a given pressure in a lean fluid compared to a richer fluid.

Ahmed et al. (2000) analyzed the effect of waterflooding in gas condensate reservoirs and compared it with gas injection. Their results showed improvement in gas and condensate production rates for both gas and water injection. Although gas injection showed higher condensate recovery factors, the authors suggest that gas injection may not be economical due to the large initial investment required, higher operating costs, and delay of gas sales. They further show that, if water injection is planned to be used in gas condensate reservoirs, the reservoir should be blown-down before water invades the majority of the producing wells and increases the water cut. Blow-down also helps re-mobilize some of the gas trapped by the injected water.

Cullick et al. (1989 and 1993) performed simulation and experimental studies to investigate the efficiency of WAG to improve recovery from gas condensate reservoirs. They proposed to use WAG instead of dry gas injection in the full pressure maintenance process and also as an alternative to early blowdown. Their results show an improvement of about 28% to 54% in total recovery over that with continuous gas injection for full pressure maintenance.
Du et al. (2000), Walker et al. (2000) and Al-Anazi (2002 and 2003) investigated the use of methanol to treat damage due to condensate and water blocking. The authors show that an enhanced flow period is observed in both low and high permeability cores after methanol treatment, during which condensate accumulation is delayed. Their experiments show:

- Significant improvement in oil and gas relative permeability is observed during the enhanced flow period after to methanol treatment. Also, the treatment is more effective in presence of high water saturation as methanol effectively removes the damage due to water blocking in addition to treating the damage due to condensate dropout.

- Significant improvement due to methanol treatment is achieved only till certain volume of methanol injection, after which the relative improvement is negligible or reduces significantly.

Methanol treatments remove both water and condensate by a multi-contact miscible displacement if sufficient methanol is injected. Methanol treatments resulted in a significant but temporary enhancement in productivity for both low and high permeability cores. However, removal of water-blocks would be expected to have a long lasting impact on a well’s PI.

Al-Anazi et al. (2003) reported successful methanol treatment to improve productivity from gas condensate Hatter's Pond field in Alabama. PVT analysis performed on samples taken from the field indicated rich retrograde condensate behavior. Walker (2000) conducted compatibility tests to ensure that the injection of filtrate and methanol did not cause any damage to the core. The well chosen for treatment was producing 250 MSCFPD with 87 BPD of condensate. After methanol treatment both gas and condensate production increased by a factor of 2 to about 500 MSCFPD and 157
BPD respectively. Well tests performed on the well before and after the treatment showed improvement in total skin from 0.68 to −1.9. This indicates that the methanol treatment effectively removed the condensate/water bank near the wellbore. However, the removal of the condensate bank is only temporary as it is expected to rebuild. The results from this test indicate that the reformation of a condensate bank does not occur immediately, the reason for which is not very clear. The authors proposed that modification of the phase behavior of reservoir fluid by the residual methanol phase trapped in the pores delayed the reformation of condensate bank.

Hydraulic fracturing has been used to enhance gas productivity (Kumar, 2000, Settari et al, 1996; Barnum et al., 1995). In many wells it is possible to reduce the drawdown, i.e. increase the flowing bottom hole pressure by inducing a hydraulic fracture that significantly increases the area available to flow. This allows the well to be produced at a higher bottom hole pressure for longer periods of time thereby delaying the onset of condensate formation around the wellbore. The success of hydraulic fracture stimulation depends on the placement of sufficient quantity of proppant without changing the integrity of the formation, the rate at which fracture fluids are produced from the fracture, and the degree to which the fracture “cleans up” after the treatment.

Settari et al. (1996) conducted a simulation study to investigate the improvement of PI due to hydraulic fracturing in the Smorbukk field. Their results show that fracturing can restore 50-70 % of the PI loss due to condensate blocking compared to a non-fractured well in a low permeability zone. In higher permeability zones, fracturing can increase the PI more than the single phase PI. They found that PI improvement is more sensitive to the fracture length in low permeability zones, whereas PI is more sensitive to the fracture conductivity in high permeability zones.
Kumar (2000) studied the effect of an idealized vertical fracture in a gas condensate well. The author predicted that for two-phase flow of gas and condensate, the productivity of a fractured well can be as high as eight times the productivity of an unfractured well. Lolon et al. (2003) showed that the fracturing fluid that remains in the fracture and formation after a hydraulic fracture treatment blocks the gas flow into the fracture and thus reduces the effective fracture length. Pressure transient tests performed on hydraulically fractured wells also support this and reveal that the effective fracture half-lengths are substantially less than the designed length from fracture stimulation. Thus the predictions from simulating idealized fractures are too optimistic.

Al-Hashim et al. (2000) performed a simulation study to investigate the improvement of PI in gas condensate wells, both above and below the dew point, due to fracturing. The authors show that hydraulic fracturing increases the time at which the dew point pressure is reached during depletion as compared to the non-fractured base case.

Li and Firoozabadi (2000) proposed to enhance the gas condensate well deliverability by altering the wettability of the near wellbore region from strong liquid wetting to preferential gas wetting. They used chemicals FC 754 and FC 722 (from 3M chemical) to alter wettability and showed that permanent gas wetting can be established in Berea and chalk through chemical treatment.

Tang and Firoozabadi (2002 and 2003) used chemicals FC 759 and FC 722 to alter the wettability from strong liquid wetting to intermediate gas wetting. These chemicals have a fluorochemical group that provides water and oil repellency, a silanol group that chemically bonds to the rock surface provides a durable treatment. The authors concluded from their experiments that treatment with the chemical FC759 can yield:

- Wettability alteration from strong liquid wetting to stable intermediate gas wetting at room temperature as well as at high temperatures.
• Neutral wetting for gas, oil, and water phases in two-phase flow
• A significant increase in oil mobility for a gas/oil system
• Improved recovery behavior for both gas/oil and oil/water systems.

2.4 Modeling of Gas Condensate Well Deliverability:

Many experimental studies have shown the effect of interfacial tension on the gas relative permeability. However, Brownell and Katz (1947) and others recognized early on that residual saturations and relative permeabilities should be a function of the ratio of viscous to interfacial forces, defined as capillary number. In some cases buoyancy forces also can be significant on the trapped phase. To account for this, the Bond number was defined as the ratio of the buoyancy forces to the interfacial forces, which also contributed to the total force on the trapped phase (Bardon and Longeron, 1980). Capillary number and the Bond number were combined using the vector sum of the forces on the trapped phase (condensate) to give the trapping number (Jin, 1995).

Pope et al. (2000) developed a trapping number dependent relative permeability model. The authors showed that this model could be used to fit typical relative permeability data available in the literature at that time. Narayanaswami et al. (1998 and 1999) proposed an analytical approach to calculate the non-Darcy flow coefficient for heterogeneous reservoirs. The authors successfully history matched the production from a gas condensate well of Arun field with the use of capillary number dependent relative permeability curves, instead of straight line relative permeability curves, and proper modeling of non-Darcy flow effects. Mott et al. (2000) showed that the inertial flow coefficient in a 3-phase gas–condensate-water system is about 50% higher then in the equivalent 2-phase gas-water system.
Civan et al. (2001) published an analytical correlation for deposition under non-equilibrium conditions. They concluded that the difference in condensate accumulation (with and without considering non-equilibrium effects), which is significant initially decreases with dimensionless time.

Al-Anazi (2003) showed from his experiments that non-equilibrium phenomenon is important at high flow rates, which represents the conditions prevailing in the near wellbore region. Rai (2003) simulated core flood experiments done by Al-Anazi (2003) using UTCOMP. Non-equilibrium effects were found to be significant at high flow rates.

Sharma (2003) studied the decline in productivity due to condensate build up on a well in the Hatter's Pond gas-condensate reservoir. The author also developed a new hybrid well model that captured the near well behavior accurately and was much faster than fine-grid simulation.

Fevang and Whitson (1996) proposed a pseudo pressure approach to model the deliverability of gas-condensate wells. They calculated the pseudo pressures and used them to calculate the well deliverability. The producing GOR, reservoir fluid PVT properties (modified black oil or compositional) and gas-oil relative permeabilities are needed to calculate the pseudo pressures.

Mott (2002) devised a new method to forecast performance from gas condensate wells using simple technique that can be used in a spreadsheet. The method uses a material balance model for reservoir depletion and two-phase pseudo pressure integral to for inflow performance. The author implemented the method in both modified black-oil and compositional simulators.

Chowdhury et al. (2004) developed a semi analytical model to accurately predict the gas and condensate production rates. The new semi-analytical model is based on ideas similar to the Fevang-Whitson-Mott pseudo pressure approach. In this method the steady
state rates are calculated analytically for grid blocks with wells and used to replace the coarse grid approximation for these grid blocks to improve the accuracy of the gas and oil production well rates.

2.5 Phase Behavior Studies of Gas Condensate Fluids

The phase behavior of gas condensate fluids is an important factor controlling the reservoir performance of gas condensate fields. Phase behavior study of gas condensate fluids can be grouped into two main categories:

- Experimental phase behavior study of gas condensate fluids.
- Modeling the PVT properties of gas condensate fluids accurately using an equation-of-state (EOS) or other correlation.

Ahmed (1986) did a comprehensive study using eight EOS models to model gas condensate systems. The equations of state used were: Peng–Robinson (1976), Soave-Redlich-Kwong (1976), the Schmidt-Wenzel (1980), the Usdin-McAuliff (1976), the Heyen, the Kubic (1983), the Adachi-Lu (1984) and the Patel-Teja (1982). Experimental data of four gas condensate hydrocarbon mixtures were compared with the predicted PVT properties from the above-mentioned equations of state. The author concluded from his studies that the Schmidt-Wenzel EOS gave a better prediction of the volumetric properties than the others. Reliable compressibility predictions were obtained from Patel-Teja and Schmidt-Wenzel EOS. Peng-Robinson, Patel-Teja and Schmidt-Wenzel equations were found to give good vapor-liquid equilibrium predictions.

Sarkar et al. (1991) used the modified Patel-Teja equation of state to model gas condensate fluid phase behavior. In their approach, the modified Zudkevitch and Joffe method was applied to determine the parameters of the EOS. The authors show better
prediction of the dew point and the condensate volume for the cases studied, using the
modified Patel-Teja EOS without using any binary interaction parameters compared to
the Patel-Teja, Peng-Robinson and ZJRK (Redlich-Kwong EOS with Zudkevitch and
Joffe method) equation of states using binary interaction parameters.

Wang et al. (2000) gave an optimized procedure for tuning the equation of state
parameters to match the experimental phase behavior of gas condensate fluid so as to be
used in reservoir simulations for more accurate well deliverability calculations.

Elsharkawy et al. (2000), using compositional analysis from 1200 compositions of
gas condensates, evaluated several methods for estimating two-phase compressibility
factors for gas condensates. The authors based their study on the large data set of gas
condensate fluids and proposed a new method to calculate the pseudo-critical properties
of the gas condensate fluids, which can be used in turn to calculate the compressibility
factors for gas condensates.

Arcia et al. (2004) developed a simplistic approach to determine the saturation
pressure based on easily acquired downhole data. The method is applicable to black oil,
volatile oil and gas condensate types of fluids where the reservoir and bottomhole
pressures are above saturation pressure and no free water is produced from the reservoir.
The dynamic pressure profile of a producing well is recorded using a pressure gauge. The
recorded pressure profile is then analyzed to establish pressure gradients, density and
gradient derivative in the wellbore and this, in turn, is interpreted in terms of
condensation, segregation, fluid convection and flow regime identification in the
wellbore. The inflection point of the gradient plot corresponds to the saturation pressure.
The dew point pressure obtained from this method was verified using the PVT analysis in
laboratory and EOS calculations.
Kokal et al. (2001) performed an experimental phase behavior study for a Saudi Arabian gas condensate fluid with water/brine. For the dry gas condensate (without water) studied, there was not a significant effect of temperature on the dew point. However, there was a significant effect on the liquid dropout; the liquid dropout reduced significantly with the increase in temperature. For the gas condensate-water system studied, the dew point pressure decreased slightly and the amount of liquid dropout increased slightly with increasing water/condensate ratio. Phase behavior of gas condensate-water mixtures was modeled using SRKEOS and reasonable agreement was obtained between the calculated and experimental results.

Lindeloff et al. (2001) and Pederson et al. (1996) proposed a thermodynamic model that can account for polar interactions and an algorithm that can generate the phase diagram for gas condensate-water systems. The model applies the Huron-Vidal method for gas condensate-water systems. Huron-Vidal (1979) derived a procedure that enables incorporating any excess Gibbs energy model, such as UNIQUAC or NRTL, into an equation of state like SRK. The authors modified the Huron-Vidal mixing rule for temperature variation. The model allows proper description of the behavior of the polar compounds while maintaining the classical model for the hydrocarbon compounds. Lindeloff et al. (2001) describes an algorithm to calculate the phase boundaries on a P-T diagram that separate the 1, 2 and 3 phase regions. The method is incorporated in the PVT SIM software provided by Calsep.

Ayyalasomyajula et al. (2002) used SAFT (Statistical Associating Fluid Theory) equation of state to model gas condensate-water-methanol mixtures. SAFT equation of state is based on statistical mechanical theories and takes into account the intermolecular potential function. It captures the major effect of non-spherical nature and association among molecules by a modified definition for the compressibility factor. The authors
show that for the pure hydrocarbon gas condensate mixture Peng-Robinson EOS gave better results than the SAFT EOS. However, for the gas condensate-methanol mixtures, after regressing both the equation of states to match the experimental data, the binary interaction parameters showed less dependence on temperature for the SAFT EOS than that for PREOS. Overall, the authors concluded that the predictions from SAFT EOS are more accurate than those from PREOS for the phase behavior of studied mixtures.

Pederson et al. (2004) studied the effect of salt on the mutual solubility of water and gas condensate mixtures over a wide range of temperatures and pressures. Their results show that the dissolved salts reduce the gas solubility in water, which is in agreement with the results of Kokal et al (2001). The gas solubility in water phase is reduced because the presence of salt in water lowers the mole fraction and fugacity coefficient of the water phase. The lowering of mole fraction is dependent on the concentration of salt and the lowering of fugacity coefficient depends on ion-water interactions. Their results also show that the mole fraction of water in the hydrocarbon phase, in equilibrium with water or brine, can be significant at high temperatures and pressures and is not sensitive to salt concentration of around 3.5mole percent. The authors modeled the phase behavior of these mixtures using SRK and PR equations of state with the Huron-Vidal mixing rules. For modeling, ions were treated as hypothetical molecules with critical properties close to glycols.
Figure 2.1: Gas relative permeability expressed as a function of capillary number for $k_{rg}/k_{ro}=1$.

Figure 2.2: Gas relative permeability expressed as a function of capillary number for $k_{rg}/k_{ro}=10$. 
Figure 2.3: Gas relative permeability expressed as a function of $k_{rg}/k_{ro}$. 
Chapter 3: Experimental Apparatus and Procedure

This chapter describes the high-pressure and high-temperature apparatus used for the phase behavior studies of hydrocarbon-water-alcohol mixtures at reservoir conditions. The gas mixture preparation methods and the constant composition expansion method to study the PVT properties of the fluid mixtures has been described in the later sections of the chapter. In the later sections the PVT software and the equation of state used for modeling the PVT properties of the fluid has been described. The chapter also gives the description of the classical van der Waals mixing rules and Huron-Vidal mixing rules used in the equation of state calculations.

3.1 EXPERIMENTAL APPARATUS:

3.1.1 Chemicals:

Hydrocarbons:

The synthetic gas mixtures used in these studies were prepared using four hydrocarbons: methane (CH$_4$), n-butane (C$_4$H$_{10}$), n-heptane (C$_7$H$_{16}$) and n-decane (C$_{10}$H$_{22}$). Research grade methane with 99.99-mol% purity, supplied in high-pressure tanks by Air-Liquid, was used in these studies. Normal butane was from Matheson in a 20-pound tank with 99.6 mol% purity. The heavier hydrocarbons, normal heptane and normal decane, were supplied by Fisher Scientific Co. at ambient conditions in bottles with 99 mol% purity.
**Alcohols:**

Two alcohols were used in these experiments: methanol and iso-propanol (IPA). Fischer Scientific Co. supplied both the alcohols at ambient conditions in 1-gallon bottles with 99 mol% purity.

**Surfactants:**

Fluorosurfactants, FC 4432 from 3M Chemicals and S10 from Solvay Solexis were used to study the phase behavior of hydrocarbon-water-methanol-fluorosurfactant phase behavior.

**Water:**

De-ionized water was used in all these experiments. The tap water was de-ionized using Barnstead de-ionizer.

### 3.1.2 Apparatus:

This section describes the various equipments used in the experimental phase behavior study of hydrocarbon-alcohol-water mixtures at high-temperatures and high-pressures.

**PVT Cell:**

A high-temperature high-pressure DBR PVT Cell was used in these experiments to study the phase behavior and fluid properties. The cell is rated for a working pressure of 10,000 psig at 329°F (200°C). The cell has a transparent glass cylinder, which contains the process fluid under study. The glass cylinder is secured between two full-length sight glass windows. The space around the glass tube is filled with transparent silicone oil, which has the same refractive index as the glass. Silicone oil is used to exert an
overburden stress on the glass, equal and opposite to the pressure on the fluid under study. This maintains zero differential pressure across the glass tube.

The glass tube has an isolation piston that obviates the need of mercury as the displacement medium. The volume of the glass tube above the isolation piston is called the sample chamber. The internal diameter of the glass tube is 1.251 inches and the total volume with and without the isolation piston are 130 ml and 152 ml, respectively. The length of the glass tube is 8.000 inches. Therefore, the glass tube constant is 7.928 ml/inch i.e. one inch of height viewed in the glass tube corresponds to 7.928 ml.

The cell has a magnetic mixer assembly mounted on one of the end cap. The magnetic mixer significantly reduces the equilibration time between the phases and thus obviates the need to oscillate or rock the cell. A benchtop control unit controls the speed and direction of the mixer.

**Pumps:**

Four types of pumps were used in these experiments: Ruska motorized positive displacement pump, Ruska digital positive displacement pump, Temco hand pump and a vacuum pump.

Ruska motorized positive displacement pumps are driven by positive gear transmissions and are capable of delivering at rates ranging from 1 cc/hr to 224 cc/hr. Ruska motorized positive displacement pump are of two types: single cylinder and dual cylinder. Each injection cylinder has a volume of 500 cc and has a vernier dial attached to it. The volume measurement can be made within accuracy of +/- 0.1 cc using these vernier dials. These pumps are rated for a pressure range of 0 to 10,000 psig.

The Ruska digital positive displacement pump is driven by a D.C. servomotor. The servo motor is equipped with a resolver that ensures displacement of the exact volume at a very precise flow rate ranging from 0.1 cc/min to 8 cc/min. The volume
measurements can be made with an accuracy of +/- 0.001 cc. The pump has a digital display which shows the flow rate and the volume injected or retracted. The pump has a single cylinder with a volume of 1000 cc and is rated for a pressure range of 0 to 5000 psig.

Temco hand pump has an injection cylinder with a volume of 250 cc and is rated for pressure up to 10,000 psig. The volume measurements can be made with an accuracy of +/- 0.01cc.

Vacuum pump from Central scientific equipments was used to vacuum equipment.

Accumulators:

High-pressure and high-temperature stainless steel accumulators from Temco, Inc. were used in these experiments. These accumulators have a volume of 1000 cc and have been pressure tested up to 7500 psig. These have a Teflon floating piston that isolates the test fluid from the pressurizing fluid.

Cathetometer:

Cathetometer from Gaerntner Scientific Co. was used in these experiments to measure the height of different phases in the PVT cell. It has a sliding lens with an adjustable focal length. The height can be measured with an accuracy of +/- 0.005 cm.

3.2 Experimental Setup

A high pressure-high temperature laboratory was setup for performing PVT experiments at reservoir conditions. Figure 3.1 shows the schematic of the experimental setup for the PVT experiments. The PVT cell was placed facing sidewalls of the oven for safety reasons. Mirrors were placed at 45° and 135° to the PVT Cell window on the front
and the rear side of the cell. The light source was kept outside the oven since the oven
temperature was raised as high as 300ºF. The light from the light source is made incident
on the front mirror. The mirror reflects the light rays through the cell and the rays are
reflected back to the observer by the rear mirror. The fluid levels were observed using the
cathetometer. The accumulators were connected to the Ruska pump and the PVT cell was
connected to the digital Ruska pump. The cell temperature was measured using a
thermocouple attached to the PVT cell end cap.

3.3 EXPERIMENTAL PROCEDURE

3.3.1 Gas Mixture Preparation:

Two different four-component synthetic gas mixtures were used in these studies.
Different gas mixtures were designed to study the phase behavior of gas condensate
hydrocarbon-water-alcohol mixtures over a wide range of temperature. The compositions
of the mixtures are given in Tables 3.1.

Two methods were followed to prepare the synthetic gas mixtures: preparing the
gas mixture in the accumulator on mass basis and preparing the gas mixture in the PVT
cell.

Gas mixture preparation in accumulator:

This method is based on preparing the synthetic gas mixture purely on mass basis.
Preparing the gas mixture on mass basis is both more accurate and simpler compared to
the method used by Walker (2000) and Al-Anazi (2003). In this method, the amount of
each component is calculated in terms of mass from their molecular weights and number
of moles only and is independent of temperature and pressure. In the method used by
Walker and Al-Anazi, the volumes of the lighter hydrocarbons, C1 and n-C4, needed to
mix the desired number of moles of each component were calculated from the Peng-Robinson equation of state at a particular temperature and pressure and they neglected to account for the volume shift correction, which meant their density was not very accurate. Also, if the pressure or temperature of the injected component is slightly off from those used for the calculations, substantial error can be made in the number of moles of the component injected to make the mixture. On the other hand, when prepared on mass basis, the accuracy in the calculation of the amount of each component is limited only by the accuracy of the weighing balance and manual errors.

For preparing the gas mixture, a high-pressure high-temperature accumulator was cleaned and vacuumed. The o-rings on the end caps and on the piston were replaced. A fixed mass of methane was taken as the reference. From the molecular weight of methane the moles of methane corresponding to the reference mass were calculated. Total moles of the gas mixture were then calculated from the calculated moles of methane and the mole fraction of methane in the gas mixture. From the total moles of gas mixture, moles of each component were calculated corresponding to their mole fractions. The mass of n-C4, n-C7 and n-C10 were then determined from their corresponding number of moles and molecular weight.

The cleaned and vacuumed accumulator is placed on the weighing balance and the weighing scale is then reset to zero. The determined mass of n-C7 and n-C10 are weighed, mixed and poured in a burette. The weighed liquid hydrocarbons are then flushed through the burette nozzle and the tube connected to the burette to get rid of any air bubble. The dispensed liquid is then returned back into the remaining mixture in the burette. The burette is then connected to the vacuumed accumulator and the liquid hydrocarbons are transferred from the burette to the accumulator slowly and carefully.
making sure that no air goes into the accumulator. The final mass of the accumulator is measured to make sure the right mass of liquid is transferred into the accumulator.

Normal butane was supplied in the form of liquid at 20-pounds by Matheson Co. The n-butane was injected using the hand pump. The hand pump was emptied and vacuumed. Then it was connected to the n-butane source tank and left for 30 min to fill with n-butane. The filled hand pump was then connected to the accumulator. The weighing scale with the accumulator and the heavier liquid hydrocarbons in it, was reset to zero. The n-butane is then slowly injected into the accumulator using the hand pump. The mass of the fluid entering the accumulator is carefully monitored on the weighing scale display to make sure the right amount of n-C4 is transferred into the accumulator. After injecting the required amount of n-C4, the hand pump was disconnected from the accumulator and the final weight of the accumulator was measured.

Methane was supplied in high-pressure tank. The high-pressure methane tank was connected to the accumulator. The weighing scale with the accumulator and the heavier liquid hydrocarbons and n-C4 in it, is reset to zero. Then using the pressure regulator on the methane tank, methane is slowly injected into the accumulator. Again while injecting methane the mass of the accumulator is carefully monitored on the weighing scale display to make sure that the right amount of methane is injected in the accumulator. Once the required mass of methane is injected, the valve on the accumulator is closed and the accumulator is disconnected from the methane tank. The final weight of the tank is again measured to make sure that the required amount of methane has been injected in the accumulator.

After injecting all the components, the accumulator is rocked to mix the components and then placed in the oven, set at the experimental temperature. The pressure of the mixture is then raised above the dew point pressure using the Ruska
pump. The mixture at high temperature and high pressure is left for 24 hrs to equilibrate and go to single phase. The accumulator is again rocked before charging the gas mixture into the PVT cell for phase behavior experiments.

**Gas mixture preparation in the PVT cell:**

The principle of preparing gas mixture in the PVT cell is similar to that followed by Walker (2000) and Al-Anazi (2003). The heavier hydrocarbons, n-C7 and n-C10, are injected on mass basis and the other two components, n-C4 and C1, are injected on volume basis. Preparing the gas mixture in the PVT cell has the advantage that the amount of each component injected in the PVT cell can be measured and corrected if the amounts are off from the calculated amount.

Gas mixture was prepared using the following procedure. The sample chamber of the PVT cell was cleaned and vacuumed. To calculate the amount of each component, a fixed volume of methane was taken as the reference. Number of moles corresponding to this volume of methane at a 1300 psig and 25°C were calculated using PR78 Peneloux (T) EOS in PVT SIM. From the number of moles of methane, the total moles of the gas mixture and the number of moles of the other components were calculated using their desired mole fractions. The amount of n-C7 and n-C10 in mass was determined from their number of moles and molecular weight. The volume of n-C4 was calculated from its number of moles and molar volume at 1000 psig and 25°C. The density of n-C4 was calculated from the PR78 Peneloux (T) EOS with the temperature-dependent volume shift correction applied. The density calculations from the EOS for n-C4 were also verified by comparison with experimental data. Table 3.2 shows the comparison of the density calculated from the EOS with and without VSP and the experimental data (Younglove, 1987). The volume shift correction significantly improves the accuracy of the calculation.
The amounts of n-C10 and n-C7 were measured, mixed and poured into a burette. The weighed liquid hydrocarbons are then flushed through the burette nozzle and the tube connected to the burette to get rid of any air bubble. The dispensed liquid is then returned back into the remaining mixture in the burette. The burette is then connected to the vacuumed sample chamber of the PVT cell and the liquid hydrocarbons, n-C7 and n-C10, were transferred into the sample chamber with special care taken to ensure it was air free.

Normal butane, supplied in 20-pound tanks, and methane, supplied in high-pressure tanks, was transferred into two separate vacuumed accumulators. The n-butane and methane accumulators were pressurized to 1000 psig and 1300 psig, respectively, using a Ruska pump. The pressurized n-butane accumulator was first connected to the PVT cell. The sample chamber of the PVT cell was also pressurized to 1000 psig using the Ruska digital positive displacement pump. The n-butane source was then opened to the sample chamber and the desired volume of n-butane was charged into the cell. The Ruska digital positive displacement pump was retrated at the same rate as the Ruska pump charged n-butane into the cell, so that the pressure is constant at 1000 psig during the injection of n-butane into the cell. After injecting the required amount of n-butane, the butane accumulator was disconnected and the methane accumulator was connected to the PVT cell. The PVT cell was pressurized to 1300 psig. The methane source was then opened to the sample chamber and the desired amount of methane was transferred into the sample chamber in a similar way as for n-butane. The accumulator was then disconnected from the PVT cell and the components in the PVT cell were mixed using a mixer. The oven with the cell is raised to the experimental temperature and the cell was pressurized above the dew point at that temperature. The gas mixture was left for 12 hours at high temperature and high pressure to equilibrate. The gas mixture was again mixed using the mixer for 30 min to get a uniform single-phase gas mixture in the cell.
3.3.2 Dead Volume Measurement for the PVT Cell:

The volume of the tubing and valves attached to the PVT cell needs to be accounted for when injecting fluids into the cell. Also, the volume of the mixer needs to be accounted for. To measure the dead volume, a known volume of water was pumped into the cell using the Ruska pump. After pumping a known volume, the volume of water in the sample chamber of the PVT cell was measured using the cathetometer. The difference between the volume of water pumped and the volume of water measured in the PVT cell gives the dead volume.

3.3.3 Constant Composition Expansion Experiment:

Constant composition expansion measurements of the fluid mixture were performed using the through-window DBR PVT cell. The desired volume of the fluid mixture under study was charged or prepared in the PVT cell as described above. The pressure in the cell was raised above the saturation pressure at the experimental temperature. For fluid mixtures with water and alcohol, the sample in the PVT cell sometimes did not go to single phase, so the pressure of the mixture was raised to 4600 psig. The pressure was then decreased gradually in small steps of 50-200 psig, by drawing silicone oil from the bottom using the Ruska digital positive displacement pump. Phase volumes were measured using the cathetometer at each pressure.

For the hydrocarbon mixtures, when the dew point was approached the single-phase gas started to turn foggy. The pressure was then decreased in steps of 10-20 psig. The fog started turning to a golden/brown color; as the dewpoint pressure was approached. At the dewpoint pressure the gas mixture turned to a dark golden/brown color and on further decrease of pressure formed two phases. The mixer in the PVT cell was used to expedite the mass transfer between phases. After the dewpoint pressure was determined, the pressure was gradually decreased in steps of 50-200 psig. The fluids in
the cell were left to equilibrate for at least 45 min and when the pressure of the cell did not change with time, the hydrocarbon liquid volume was measured. The assumption was made that the liquid and the vapor phase approximately attained equilibrium in this period of time with the help of the mixer. The liquid dropout of the mixture was calculated as:

\[
LDO\% = \frac{V_l}{V_t} \times 100
\]

Eq. 3.1

where, \( V_l \) is the volume of liquid (condensate) collected at a given pressure, and \( V_t \) is the total volume of the gas mixture (gas and condensate) at this pressure.

For hydrocarbon-alcohol-water mixtures, sometimes the mixture in the PVT cell had two phases even at high pressures. For such mixtures the saturation pressure measured was the three-phase saturation pressure where two incipient phases flash into three phases. The pressure on the mixture in the cell was decreased gradually in steps till the mixture reaches the 3-phase saturation point. At this 3-phase saturation point, the Liquid-Vapor (L-V) or Liquid-Liquid (L-L) mixture flashed into Liquid-Liquid-Vapor (L-L-V) mixture. The heavier liquid phase was mainly made up of component water and will be referred as the aqueous phase. The lighter liquid phase had mostly heavier hydrocarbon components and will be referred to as the liquid hydrocarbon phase. The pressure on the fluid mixture was further decreased in steps of 50-200 psig and phase volumes were measured. To attain equilibrium between the phases, the fluids in the cell were left in the cell for 45 min to 1hr at each pressure step. The phase volume % was calculated as:

\[
\text{Phase volume } \% = \frac{V_i}{V_t} \times 100
\]

Eq. 3.2
Where, $V_i$ is the phase volume, $i$ represents vapor, liquid or aqueous phase, and $V_t$ is the total volume of the mixture at that pressure.

3.4 PVT SOFTWARE

PVTSim, a PVT software package provided by Calsep Inc., was used for the phase behavior modeling. The original and the modified forms of the equation of state models by Peng-Robinson and Soave-Redlich-Kwong have been incorporated into the software package. The software can handle both polar and non-polar molecules as it provides an option for the type of mixing rule to be used. An important feature of the software is that it can perform three-phase flash and calculate three-phase pressure-temperature phase diagrams. The algorithm for calculating two- and three-phase boundaries for the pressure-temperature phase diagrams was given by Lindeloff and Michelson (2002).

The software provides an option for simulating various PVT operations, calculation of minimum miscibility pressure for gas injection, simulation of hydrates and asphaltenes. PVTSim also provides an option for regressing the equation of state parameters to match the experimentally measured constant composition expansion (CCE), constant volume depletion (CVD) and other PVT experimental data.

3.5 EQUATION OF STATE

Peng-Robinson EOS, a cubic EOS developed by Peng and Robinson in 1976, has been shown to accurately model hydrocarbons and is the most widely used EOS in compositional reservoir simulators.

The PREOS is expressed as -
\[
P = \frac{RT}{V - b} - \frac{a(T)}{V(V + b) + b(V - b)} \quad \text{Eq. 3.3}
\]

where
\[
a(T) = a_c \alpha(T) \quad \text{Eq. 3.4}
\]
\[
a_c = \Omega_c \frac{R^2 T_c^2}{P_c} \quad \text{Eq. 3.5}
\]
\[
\alpha(T) = \left[ 1 + m \left( 1 - \left( \frac{T}{T_c} \right)^{0.5} \right) \right]^2 \quad \text{Eq. 3.6}
\]
\[
b = \Omega_b \frac{RT_c}{P_c} \quad \text{Eq. 3.7}
\]

and
\[
\Omega_c = 0.45724 \\
\Omega_b = 0.07780 \quad \text{Eq. 3.8}
\]

The parameter \( m \) for PREOS is found from
\[
m = 0.37464 + 1.54226 \omega - 0.269922 \omega^2 \quad \text{Eq. 3.9}
\]

The Peng-Robinson EOS was modified in 1978 and is known as PR78 EOS. For PR78 equation \( m \) is found from the same correlation (Eq 3.9.) if \( \omega \leq 0.49 \). Otherwise the below correlation is used
\[
m = 0.379642 + \omega(1.48503 - 0.164423 \omega + 0.01666 \omega^2) \quad \text{Eq. 3.10}
\]

With Peneloux volume correction the PR78 equation of state becomes
\[
P = \frac{RT}{V - b} - \frac{a(T)}{(V + c)(V + 2c + b) + (b + c)(V - b)} \quad \text{Eq. 3.11}
\]

where \( c \) is known as Peneloux volume correction and is defined as the difference between the Peneloux molar volume and the molar volume calculated without Peneloux volume correction. The parameter \( c \) is expressed as the sum of a temperature independent
volume correction \((c')\) and a temperature dependent volume correction \((c'')\) in PVTSim software:

\[
c = c' + c''(T - 288.15)
\]

Eq. 3.12

where \(T\) is the temperature in K.

The temperature independent volume correction for PR78 is calculated from

\[
c' = 0.50033 \frac{RT_c}{P_c} (0.25969 - Z_{RA})
\]

Eq. 3.13

where \(Z_{RA}\) is the Racket compressibility factor and is calculated as:

\[
Z_{RA} = 0.29056 - 0.08775\omega
\]

Eq. 3.14

The PR78 EOS with temperature dependent Peneloux volume correction will be referred as PR78 Peneloux \((T)\) EOS in the further sections.

The most common mixing rules used for non-polar mixtures are the classical van der Waals mixing rules. The mixing rules are based on one binary interaction parameter per pair. The parameters \(a\), \(b\) and \(c\) for the mixture are calculated as:

\[
a = \sum_{i=1}^{N} \sum_{j=1}^{N} z_i z_j a_{ij}
\]

\[
b = \sum_{i=1}^{N} z_i b_i
\]

Eq. 3.15

\[
c = \sum_{i=1}^{N} z_i c_i
\]

where \(z_i\) and \(z_j\) are mole fractions, \(i\) and \(j\) component indices, and

\[
a_{ij} = \sqrt{a_i a_j} (1 - k_{ij})
\]

Eq. 3.16

where \(k_{ij}\) is the binary interaction parameter between component \(i\) and \(j\).
Mixtures with one or more polar components exhibit a great degree of non-ideal behavior. Therefore, EOS models with mixing rules that are capable of describing a greater degree of non-ideality than is possible with van der Waals classical mixing rules are required. The most common approach to model such mixtures has been by developing better mixing rules by combining an EOS with activity coefficient models. Huron and Vidal (1979) have developed such a model that incorporates activity coefficient model in a cubic equation of state. They defined the parameter 'a' of mixing rules in such a manner that conventional mixing rule can be recovered for the hydrocarbon-hydrocarbon interactions. The Huron and Vidal a-parameter mixing rule takes the form:

\[ a = b \left( \sum_{i=1}^{N} \left( z_{i} \frac{a_{i}}{b_{i}} \right) - \frac{G_{E}^{\infty}}{\lambda} \right) \]  

Eq. 3.17

where \( \lambda \) for PREOS is given by

\[ \lambda = \frac{1}{2} \ln \left( \frac{\sqrt{2}+1}{\sqrt{2}-1} \right) \]  

Eq. 3.18

\( G_{E}^{\infty} \) is the Gibbs energy at infinite pressure and is found using a modified NRTL mixing rule

\[ \frac{G_{E}^{\infty}}{RT} = \sum_{i=1}^{N} \frac{\tau_{ij} b_{i} z_{i} \exp(-\alpha_{ij} \tau_{ij})}{\sum_{k=1}^{N} b_{k} z_{k} \exp(-\alpha_{ki} \tau_{ki})} \]  

Eq. 3.19

\( a_{ij} \) is a non-randomness parameter to account for the local composition effects as local mole fraction may differ from overall mole fraction. The parameter \( \tau_{ij} \) accounts for the interaction between molecules via the following expression

\[ \tau_{ij} = \frac{g_{ji} - g_{ii}}{RT} \]  

Eq. 3.20

where \( g_{ji} \) is an energy parameter characteristic of the j-i interaction. In PVTSim the g parameters are temperature dependent and given by the expression (Pederson et al., 2001)
\[ g_{ij} - g_{ii} = (g_{ij} - g_{ii})' + T(g_{ij} - g_{ii})'' \]

where \((g_{ij} - g_{ii})'\) and \((g_{ij} - g_{ii})''\) are temperature independent parameters.

Huron-Vidal mixing rule can be reduced to the classical mixing rule when the parameters \(\alpha\) and \(g\) are selected as follows

\[ \alpha_{ij} = 0 \]

\[ g_{ii} = -\frac{a_i}{b_i} \lambda \]

\[ g_{ij} = -2 \sqrt{b_i b_j} (g_{ij} g_{ii})^{0.5} (1 - k_{ij}) \]

This allows for the model to be applied for mixtures of hydrocarbons and polar compounds alike, allowing for a proper description of the behavior of polar compounds while maintaining the classical model for the hydrocarbon. The PR78 EOS with temperature dependent Peneloux volume correction and Huron-Vidal mixing rule will be referred as PR78 Peneloux (T)-HV EOS in further sections.
Table 3.1: Gas mixture compositions

<table>
<thead>
<tr>
<th>Components</th>
<th>Gas mixture 1</th>
<th>Gas mixture 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mole fraction</td>
<td>Mole fraction</td>
</tr>
<tr>
<td>C1</td>
<td>0.785</td>
<td>0.81</td>
</tr>
<tr>
<td>n-C4</td>
<td>0.15</td>
<td>0.05</td>
</tr>
<tr>
<td>n-C7</td>
<td>0.05</td>
<td>0.06</td>
</tr>
<tr>
<td>n-C10</td>
<td>0.015</td>
<td>0.08</td>
</tr>
</tbody>
</table>

Table 3.2: Comparison of specific volume of butane with and without volume shift correction and the experimental data.

<table>
<thead>
<tr>
<th>T=25°C</th>
<th>Specific volume cm$^3$/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure, psi</td>
<td>Experimental</td>
</tr>
<tr>
<td>1000</td>
<td>99.597</td>
</tr>
</tbody>
</table>
Figure 3.1: Schematic of the experimental setup for PVT experiments.
Chapter 4: Phase Behavior Results

4.1 INTRODUCTION

Phase behavior study of gas condensate fluids is imperative to evaluate the production performance of gas condensate fields. The presence of water in gas condensate reservoirs makes it necessary to study the effect of water on the phase behavior of the mixture. Also, the recent experimental coreflood studies done by Walker et al. (2000) and Al-Anazi (2003) and the successful field treatment of the Hatter’s Pond field have shown that methanol treatment can significantly reduce the damage caused by condensate accumulation and increase the productivity. The successful treatment of methanol has thus made it important to study the gas condensate-water-methanol phase behavior and model this behavior using equations-of-state. Very limited phase behavior studies have been done on such mixtures, and most of them have been done at low temperatures to study hydrates.

For mixtures of simple hydrocarbons, the conventional cubic EOS gives reasonably accurate phase behavior predictions. But gas condensate fluids often contain both hydrocarbon and non-hydrocarbon components, and for gas condensate-water and gas condensate-water-alcohol mixtures, which have both polar and non-polar components, the conventional cubic equations-of-state must be tuned and even then may not be accurate. This is because there are limitations such as the failure to correctly handle polar components where local composition effects dominate, and problems in correlating phase behavior over a wide temperature range. Moreover the classical van der
Waals mixing rule with a single binary interaction parameter per component pair is well suited for the description of a mixture that exhibits only modest deviation from the ideal solution behavior.

This chapter discusses the results of the experiments done to study the phase behavior of gas condensate mixtures and the effect of water and methanol on their phase behavior. The PVT data was used to tune the parameters of PR78 equation-of-state with temperature-dependent Peneloux volume shift corrections. Phase behavior calculations were done using both classical van der Waals and Huron-Vidal mixing rules.

The chapter also includes the phase behavior experiments of hydrocarbon-water-isopropanol mixtures. Comparison of the effect of isopropanol and methanol on the hydrocarbon-water mixture is also shown. Last section of the chapter discusses the effect of fluorosurfactants FC4432 and S10 on the phase behavior of hydrocarbon-water-methanol mixtures.

**4.2 LIQUID DROPOUT MEASUREMENTS FOR GAS CONDENSATE MIXTURE**

Two synthetic gas mixtures were used to study the phase behavior of gas condensate hydrocarbons over a wide range of temperature. The gas mixtures were prepared from the same components but with different molar concentrations. Table 4.1 gives the composition of gas mixture-1. Table 4.2 gives the critical properties of these components (default values in PVTSim). Walker *et al.* (2001) and Al-Anazi (2003) used the same synthetic gas mixture in their experimental core flooding study of condensate blocking. Figure 4.1 gives the phase envelope of this gas mixture calculated using the PR78 Peneloux (T) EOS. The liquid dropout of the mixture was measured using CCE method, as described in section 3.7, at 152°F. The fluid behaves as a retrograde gas condensate at this temperature.
Al-Anazi (2003) measured the liquid dropout of the same gas mixture under the same conditions, using the CCE method in a windowed PVT cell. The comparison of the two sets of measured data is given in Figure 4.2. PR78 Peneloux (T) EOS was used to calculate the liquid dropout curve for the above mixture. The binary interaction parameters between the hydrocarbon components were taken as zero. The volume shift parameters were used to get better predictions of liquid phase density. Table 4.3 gives the value of the volume shift parameters used in the calculations (default values in PVTSim). All the data and calculated liquid dropout curves are shown using the liquid volume divided by the total volume rather than the dew point volume. In order to match the experimentally measured liquid dropout data, the overall composition of the mixture was adjusted slightly. Table 4.4 gives the comparison of the original and the adjusted compositions. Figure 4.2 compares the measured data and the calculated liquid dropout curve from the equation-of-state. The result shows good agreement between the experimentally measured liquid volume fraction data and the equation-of-state calculations after minor tuning of the composition.

A new synthetic gas mixture was designed to study the phase behavior of gas condensate fluids at higher temperature. Table 4.5 gives the composition of the gas mixture-2. Figure 4.3 gives the phase envelope of the gas mixture, calculated using PR78 Peneloux (T) EOS. The liquid dropout of the mixture was measured using the CCE method at 200°F, 251.5°F and 300°F. The above temperatures were chosen for the experiments so as to move from a bubble point fluid across the critical point to a dew point fluid. The equation-of-state calculations show that the fluid mixture behaves as a volatile oil at 200°F, near critical fluid at 251.5°F and retrograde gas condensate at 300°F.

Figures 4.4, 4.5 and 4.6 compare the experimentally measured liquid volume fractions and the liquid dropout curve calculated from the equation-of-state. PR78
Peneloux (T) EOS was used to calculate the liquid dropout curve of the gas mixture-2 at the above-mentioned temperatures. Non-zero binary interaction parameters were used between the hydrocarbon components. Three different sets of binary interaction parameters between the hydrocarbon components were used for the equation-of-state calculations to match the experimental data at the above-mentioned temperatures. Tables 4.6, 4.7 and 4.8 give the binary interaction parameters for 200°F, 251.5°F and 300°F respectively.

Figure 4.7 shows the variation of the binary interaction coefficients between the components as a function of temperature. The binary interaction coefficients exhibit linear dependence on temperature. However, the values of binary interaction parameters used between hydrocarbons are negligible in the above temperature range and therefore have been assumed as zero hereafter. The volume shift parameters given in Table 4.3 were used for the equation-of-state calculations. The results show that reasonably good agreement is obtained between the experimentally measured liquid volume fractions and equation-of-state calculations using temperature-dependent binary interaction parameters. The equation-of-state over-predicts the saturation pressure at 200°F and 251.5°F.

4.3 Phase Behavior of Gas Condensate Hydrocarbon-Methanol Mixtures

Experiments were performed to study the effect of methanol on the phase behavior of gas condensate hydrocarbons. 16.67 mol% of methanol was added to gas mixture-1. The composition of the new mixture, mixture-3, is given in Table 4.9. Liquid volume fractions were measured using the CCE method at 152°F. Figure 4.8 compares the liquid dropout curve for gas mixture-1 with and without methanol at 152°F. The results show that methanol increases the dewpoint pressure by about 350 psi (actual dew
point was not measured) as well as the liquid volume fractions. Addition of methanol increased the maximum liquid dropout volume of gas mixture-1 by almost 40% of the original maximum liquid dropout i.e. from 21.49% to 29.95% of the total volume. Walker (2001) studied the effect of different mol% of methanol on the phase behavior of gas mixture-1 and obtained similar results. CCE was then performed on mixture-3 (composition given in table 4.9) at 180°F, 252°F and 301°F to see the effect of temperature on the phase behavior of gas condensate-methanol mixture. Figure 4.9 shows the measured liquid dropout curves for the mixture at 152°F, 180°F, 252°F and 301°F. As expected the liquid dropout and the dewpoint pressure decreases with increasing temperature.

PR78 Peneloux (T) EOS with classical van der Waals mixing rules was used to model the methanol-hydrocarbon mixture. Non-zero binary interaction parameters were used between hydrocarbons and methanol to account for their non-ideal interaction. The binary interaction coefficients between hydrocarbon components were assumed to be zero. The equation-of-state was regressed to match the experimentally measured liquid dropout data by tuning the binary interaction parameters between methanol and hydrocarbon components. Figure 4.9 shows the comparison of the measured liquid dropout for the mixture at the above-mentioned temperatures with the tuned equation-of-state calculations.

Table 4.10 gives the values of the binary interaction parameters used between hydrocarbons and methanol at the above-mentioned temperatures. Figure 4.10 shows the variation of binary interaction parameters between methanol and each hydrocarbon component with temperature. The result shows that binary interaction parameters exhibit linear dependence on temperature. Also, they decrease as the temperature increases since the solutions become less non-ideal as the kinetic energy of the molecules increases.
4.4 Phase Behavior of Hydrocarbon-Water Mixtures

Water is commonly associated with reservoir gas condensate fluids. Thus, the effect of water on the phase behavior of gas condensate hydrocarbons is important. To study the phase behavior of water-hydrocarbon mixtures, a new mixture was prepared with 36.24 mol% of water and 63.76 mol% of gas mixture-2. The composition of the new mixture, mixture-4, is given in Table 4.11. CCE experiment was performed on the mixture at 300°F and the phase volume fractions were measured. At 300°F and the operating pressure range, the phase behavior of the mixture is liquid-liquid-vapor (L-L-V). The heavier liquid phase is primarily water and will be referred as aqueous phase. The second liquid phase is mainly composed of heavier hydrocarbons and will be referred as liquid hydrocarbon phase. The experimentally measured phase volume fractions are shown in figure 4.11. Although the addition of water causes a third phase to form, the ratio of hydrocarbon liquid to vapor phase and the dew point pressure remain almost unaffected. This suggests that water has very little effect on the hydrocarbon phase behavior as most of the water remains in the aqueous phase and only a very small fraction of it is in the vapor phase.

PR78 Peneloux (T) EOS was tuned by adjusting the binary interaction parameters between each hydrocarbon and water and the volume shift parameter of water to match the experimental data. Table 4.12 gives the binary interaction and volume shift parameters used for the equation-of-state calculations. Figure 4.12 shows the P-T phase diagram of the mixture calculated using the equation-of-state. The figure shows the single phase, two-phase and three-phase regions. Figure 4.11 compares the measured phase volume fractions with the tuned equation-of-state calculations. The result shows a good agreement between the measured data and the tuned equation-of-state calculations.
Figure 4.13 shows the distribution of water component in all the three phases calculated using the tuned EOS. The result shows clearly that there is less than 5 mol% water in the vapor and liquid hydrocarbon phases at high pressures. At very low pressures the water mole fraction in the vapor phase increases significantly as it approaches the vapor pressure of water at 300°F (The vapor pressure of pure water at 300°F is 51.3 psig). Pederson et al. (2004) and Kokal et al. (2001) have reported similar results from their studies of hydrocarbon-water mixtures.

4.5 Phase Behavior of Hydrocarbon-Water-Methanol Mixtures

The phase behavior of hydrocarbon-water-methanol mixtures is complex and only very limited data have been published with most of the studies done at low temperatures.

CCE measurements were performed on a hydrocarbon-water-methanol mixture at 300°F. The mixture was prepared by adding 25 mol% of methanol to the hydrocarbon-water mixture given in Table 4.11. The composition of the resultant mixture, mixture-5, is given in Table 4.13. Figure 4.14 shows the measured phase volume fractions of the hydrocarbon-water-methanol mixture at 300°F. At 300°F and the operating pressure range, the phase behavior is liquid-liquid-vapor (L-L-V). The addition of methanol to the mixture reduced the dew point pressure by 310 psi compared to that of the hydrocarbon gas mixture and by 280 psi when compared to the hydrocarbon-water mixture. This result is in contrast to the results obtained for hydrocarbon-methanol mixtures, where the dewpoint pressure increased by 350 psi on adding 16.667 mol% of methanol to the gas mixture. The reason for the different results is, however, not clear at this stage.

The phase behavior measurements by CCE method also show that the phase volume fraction of the aqueous phase increases from 5% to 17% with the addition of methanol. The total liquid volume fraction increases correspondingly, but there is
negligible effect on the hydrocarbon liquid volume fraction. This result indicates that a significant amount of methanol goes to the aqueous phase.

The experimentally measured phase volume data was modeled with PR78 Peneloux (T) EOS by tuning the binary interaction coefficients between hydrocarbon-methanol and water-methanol. The binary interaction coefficient between water and each hydrocarbon used in the EOS was same as those given in table 4.12. Table 4.14 gives the binary interaction parameters and volume shift parameters used for the EOS calculations.

Figure 4.14 compares the experimentally measured phase volume data with the tuned equation-of-state calculations. Classical van der Waals mixing rules were used between all the components for the EOS calculations. The result shows an almost perfect agreement between the measured data and calculated phase volume fractions. Figure 4.15 shows the P-T phase diagram calculated using the above tuned equation-of-state. The result shows that the algorithm for P-T phase diagram calculation in PVTSim fails to calculate the entire phase diagram. However, the phase compositions and properties can be calculated using the multi-phase flash option in PVTSim.

The PR78 Peneloux (T) equation-of-state was also used with different mixing rules to match the experimental data. Since the Huron and Vidal mixing rules were developed for mixtures with at least one polar component, it was tested for phase behavior modeling of mixture-5. PVTSim software has three options for the type of mixing rule between components: classical, temperature-dependent classical and Huron-Vidal mixing rule. Huron-Vidal mixing rule was used between water and methanol and classical mixing rules between the other components. Table 4.15 gives the mixing rules used between the components. The PR78 Peneloux (T) EOS with the Huron and Vidal mixing rules between water and methanol and classical mixing rules for water-hydrocarbon, methanol-hydrocarbon and hydrocarbon-hydrocarbon interaction will be
referred as PR78-Peneloux (T)-HV below to distinguish it from the PR78-Peneloux (T) EOS. The binary interaction parameters between the components modeled with classical mixing rules were the same as those used above, given in Table 4.14. The interaction between components modeled with the Huron-Vidal mixing rule is defined by five interaction parameters per binary, which are $a_{ij}$, $g_{ij}$, $g_{ji}$, $g_{ij}(T)$ and $g_{ji}(T)$, where $g_{ij}(T)$ and $g_{ji}(T)$ are temperature dependent terms of $g_{ij}$ and $g_{ji}$. The five Huron-Vidal interaction parameters between methanol and water are given in Table 4.15. These are the default parameters in PVTSim database.

Figure 4.14 compares the phase volume fraction calculations using PR78-Peneloux (T)-HV and PR78-Peneloux (T) with the measured data. The calculations with both equations-of-state are in reasonably good agreement with the experimentally measured data. Figure 4.16 shows the P-T phase diagram calculated using the tuned PR78-Peneloux (T)-HV EOS. The phase diagram shows the single-phase, two-phase and the three-phase region for the mixture. The algorithm in PVTSim software could not calculate the critical point of the mixture. At 300°F, the phase diagram shows two phases for pressures above 3300 psig and three phases between 200 and 3300 psig.

**4.5.1 Effect of Temperature on the Phase Behavior of Hydrocarbon-Water-Methanol Mixtures:**

Phase behavior of any mixture is a strong function of temperature. Also, the equation-of-state parameters such as binary interaction parameters and volume shift parameters are temperature dependent. A new gas mixture with 25 mol% water, 25 mol% methanol and 50 mol% gas mixture-2 was used to study the effect of temperature on the phase behavior of hydrocarbon-water-methanol mixtures. The overall composition of the mixture, mixture-6, is given in Table 4.17. CCE measurements were performed on the
mixture at 200°F, 254°F and 300°F. Figures 4.17, 4.18 and 4.19 show the experimentally measured phase volume fractions at 200°F, 254°F and 300°F respectively.

At all three temperatures, there are two phases at high pressures and then the mixture flashes into three phases at the three-phase saturation pressure. The results show that the mixture is Liquid-Liquid (L-L) at 200°F above 3845 psig. At 3845 psig the mixture flashes into three phases: vapor, liquid-1 and liquid-2. The liquid-2 phase, as before, is called the aqueous phase. At 254°F the mixture is two phase, an aqueous and a hydrocarbon rich phase above 3622 psig. However, the nature of the hydrocarbon rich phase could not be determined as it behaves as a near critical fluid at this temperature and it is difficult to distinguish between the liquid and vapor phase. The mixture flashed into three phases at 3622 psig, however, the nature of the saturation point for the hydrocarbon rich phase, i.e. either bubble point or dew point, could not be determined for the before mentioned reason. At 300°F, the mixture is two-phase vapor-aqueous liquid above 3359 psig. At 3359 psig, the mixture is a three-phase vapor-liquid-aqueous liquid.

PR78 Peneloux (T) EOS was tuned by adjusting the binary interaction parameters for the hydrocarbons-methanol and water-methanol interactions to match the experimental data at each temperature. Different binary interaction parameters were used in the equation-of-state at different temperatures to get a good match with the measured data. Table 4.18 gives the binary interaction parameters used for methanol-water and methanol-hydrocarbon interactions at 200°F, 254°F and 300°F. Figure 4.20 shows the variation of these binary interaction parameters for methanol-hydrocarbon and methanol-water interactions with temperature. The result shows that these parameters are a linear function of temperature. The key parameter is the negative binary interaction parameter between methanol and water for all three temperatures. Ayyalasomayajula et al. (2002) reported similar negative binary interaction parameters between water and methanol. An
important observation is that the binary interaction parameters between methanol and hydrocarbons show a different trend with temperature compared to the values for the mixture without water (Figure 4.10). This implies that presence of water significantly affects the methanol-hydrocarbon interactions. Binary interaction parameters for water with each hydrocarbon were kept the same for all three temperatures and are given in Table 4.12.

Volume shift parameters are defined as a temperature-dependent function in PVTSim. The default values in PVTSim software for the PR78 Peneloux (T) equation-of-state were used at all three temperatures. Table 4.19 gives the volume shift parameters for the components at three temperatures. Figures 4.17, 4.18 and 4.19 compare the measured phase volume fractions and the tuned equation-of-state calculations at 200°F, 254°F and 300°F respectively. A good agreement is obtained between the measured data and the equation-of-state calculations for all three temperatures with these parameters. Figure 4.21 shows the P-T phase diagram calculated using the above tuned equation-of-state. The phase diagram shows the single-phase, two-phase and the three-phase regions.

PR78- Peneloux (T)-HV EOS was also regressed to match the experimental data at the three temperatures. The binary interaction parameters for each hydrocarbon-water and each hydrocarbon-methanol interactions for equation-of-state calculations were the same as those used in PR78 Peneloux (T) EOS. The five interaction parameters used for water and methanol interaction defined by Huron-Vidal mixing rule are given in Table 4.16.

Figures 4.17, 4.18 and 4.19 compare the tuned PR78-Peneloux (T)-HV EOS calculation with the measured data and the calculations from the tuned PR78 Peneloux (T) EOS. The calculations with both equations-of-state are in reasonably good agreement with the experimentally measured data. Figure 4.21 compares the P-T phase diagram
calculated using PR78-Peneloux (T)-HV EOS with the PR78 Peneloux (T) EOS calculations. The figure also shows the saturation pressures, on the phase boundary separating two-phase and three-phase region, measured at the 200°F, 254°F and 300°F from CCE measurements. The result shows the phase boundaries calculated by both the tuned equation-of-state are in good agreement with each other and with the measured saturation pressure data.

Figures 4.22, 4.23 and 4.24 show phase density variation for the three phases at 200°F, 254°F and 300°F with pressure using PR78 Peneloux (T) EOS and PR78-Peneloux (T)-HV EOS. The phase densities of all the three phases calculated with both equations-of-state are in almost perfect agreement. The result shows that for all three temperatures studied, the vapor phase density decreases from approximately 0.3 g/cc to 0.01 g/cc and the hydrocarbon liquid (HC liquid) phase density increases from approximately 0.3 g/cc to more than 0.6 g/cc as the pressure is decreased below the three-phase saturation pressure. Above the three-phase saturation pressure, the HC liquid phase density at 200°F and the vapor phase densities at 254°F and 300°F remain almost constant. The aqueous phase density decreases negligibly over the entire pressure range for all three temperatures.

Figures 4.25, 4.26 and 4.27 compare the methanol molar concentration in the three phases at 200°F, 254°F and 300°F respectively, calculated using PR78 Peneloux (T) EOS and PR78-Peneloux (T)-HV EOS. The result shows that the calculations from the equations-of-state agree qualitatively but shows some discrepancies quantitatively. These discrepancies increase with temperature and become significant at 300°F. At 300°F the methanol molar concentration in the vapor and hydrocarbon liquid (HC liquid) phases calculated by PR78-Peneloux (T)-HV EOS is more than those calculated by PR78 Peneloux (T) EOS whereas, the molar concentration calculated in the aqueous phase is
lower. This is probably because of the different nature of the mixing rules used for defining the water-methanol interaction. However, no compositional analysis was made to verify the equation-of-state calculations.

Thus, with these equations-of-state some properties of the mixture can be calculated accurately, but these tuned equations-of-state cannot be used to calculate all the properties with complete accuracy. For this mixture, the phase behavior, phase densities and phase diagram calculations are in agreement but the compositional analysis is different.

The tuned binary interaction parameters and volume shift parameters used in the equation-of-state for the above mixture calculates the phase behavior properties of the mixture with a reasonable accuracy over a range of temperature. However, these parameters may change with the composition of the mixture. To investigate this, phase behavior experiments with hydrocarbon-water-methanol mixtures with different water and methanol mole fractions were done.

4.5.2 Effect of Water Mole Fraction on the Phase Behavior of Hydrocarbon-Water-Methanol Mixtures:

The study of the effect of water on the phase behavior of hydrocarbons (section 4.4) showed that water does not affect the phase behavior of hydrocarbon mixtures significantly. However, the comparison of the variation of binary interaction parameters between hydrocarbons and methanol with temperature in the presence and absence of water (Figure 4.19 and 4.10 respectively) showed that water affects the phase behavior of hydrocarbon-methanol mixtures. Experiments were thus performed to get a better understanding of the effect of water mole fraction on the phase behavior of hydrocarbon-water-methanol mixtures. This section discusses the effect of water mole fraction on the phase behavior of hydrocarbon-water-methanol mixtures.
A new mixture with 50 mol% of water and 25 mol% methanol was used for this study. The total composition of the mixture, mixture-7, is given in Table 4.20. CCE measurements were performed on the mixture at 200°F, 254°F and 300°F. Figures 4.28, 4.29 and 4.30 show the experimentally measured phase volume fractions at 200°F, 254°F and 300°F respectively. The phase behavior and properties of this mixture were compared with those of mixture-6 (Table 4.16) to see the effect of water mole fraction.

Figures 4.31, 4.32 and 4.33 compares the CCE measurements done on the mixtures with 25 mol% water (mixture-6) and 50 mol% water (mixture-7) at the above-mentioned temperatures. Increasing the water mole fraction from 25 mol% to 50 mol% and keeping the mole fraction of the other components the same almost doubled the aqueous phase volume fraction at all three temperatures. This indicates that most of the added water is in the aqueous phase. Also, there was no noticeable change observed in the three-phase saturation pressure with the addition of water at the above-mentioned temperatures. These results are similar to those obtained when water was added to pure hydrocarbon gas mixture (section 4.4).

PR78 Peneloux (T) EOS and PR78 Peneloux (T)-HV EOS were used to model the mixture. Figures 4.31, 4.32 and 4.33 compares the measured phase volume fractions with the equation-of-state calculations for the mixtures with 25 mol% and 50 mol% water at 200°F, 254°F and 300°F respectively. EOS models with the same set of binary interaction parameters between components and volume shift parameters were used to model both mixtures. For PR78 Peneloux (T)-HV EOS, the same set of five interaction parameters were used between water and methanol for both the mixtures. The set of parameters used is the same as those described in section 4.5.1. The result shows that with the same set of equation-of-state parameters, good agreement is obtained between the measured phase volume fractions and the equation-of-state calculations for both the mixtures.
Figure 4.34 compares the P-T phase diagram calculated using the tuned PR78 Peneloux (T) and PR78 Peneloux (T)-HV equation-of-state. The figure also compares the measured three phase saturation pressures at 200°F, 254°F and 300°F with the three-phase phase boundary calculated using the EOS models. The result shows good agreement between the measured and calculated values of three-phase saturation pressures. Figure 4.35 compares the P-T phase diagram calculated using the above-mentioned PR78 Peneloux (T) equation-of-state model for the mixtures with 25 mol% and 50 mol% water. The phase diagram shows that the addition of water does not affect the three-phase boundary however, it shifts the two-phase boundary to the right i.e. to higher temperatures.

Figures 4.36, 4.37 and 4.38 shows the comparison of the phase densities calculated for mixture-7 using the above-mentioned equation-of-state models at 200°F, 254°F and 300°F respectively. The result shows extremely good agreement between the phase densities of all the three phases calculated using both the equation-of-state models. Comparing the phase densities calculated for mixture-6 and mixture-7 shows that the addition of water does not affect the densities of the phases significantly.

Figures 4.39, 4.40 and 4.41 show the methanol molar concentration in the three phases calculated for mixture-7 using both the equation-of-state models at 200°F, 254°F and 300°F respectively. The result shows that the calculations from both the equation-of-state models agree qualitatively but shows some discrepancies quantitatively. These discrepancies increase with temperature and become significant at 300°F. Similar discrepancies in the calculation of methanol molar concentrations were obtained for mixture-6. Figure 4.42 shows the variation of the calculated methanol mole fractions with temperature in the three phases at 1200 psig. The figure compares the methanol mole fraction calculated using both the equation-of-state models. The methanol mole
fraction in all the three phases as calculated using PR78 Peneloux (T) EOS varies almost linearly with temperature. However, those calculated using PR78 Peneloux (T)-HV EOS show large deviation from a linear relation, especially in the hydrocarbon liquid phase. The analysis suggests that the compositional analysis form PR78 Peneloux (T) EOS, i.e. using classical mixing rules between all the components is more accurate.

Comparing the methanol molar concentrations calculated for mixtures-6 and 7 shows that addition of water significantly reduces the methanol mole fraction in the aqueous phase at all the three temperatures. This is simply because most of the additional water goes in the aqueous phase and thus decreases methanol molar concentration in that phase. The methanol mole fraction is also reduced in the vapor and hydrocarbon liquid phases by the addition of water, but to a much less extent.

4.5.3 Effect of Methanol Mole Fraction on the Phase Behavior of Hydrocarbon-Water-Methanol Mixtures:

Previous two sections have discussed the effect of temperature and water mole fraction on the phase behavior of hydrocarbon-water-methanol mixtures. Methanol mole fraction is another important parameter that affects the hydrocarbon-water-methanol phase behavior. This section discusses the effect of methanol mole fraction on the phase behavior of hydrocarbon-water-methanol mixtures. The section also discusses the validity of the equation-of-state parameters obtained in the previous sections.

A new mixture with 45 mol% methanol was designed for this study. The composition of the new mixture, mixture-8, is given in Table 4.21. CCE measurements were performed on the mixture at 200°F, 254°F and 300°F. Figures 4.43, 4.44 and 4.45 show the experimentally measured phase volume fractions at 200°F, 254°F and 300°F respectively. The phase behavior and properties of this mixture were compared with those of mixture-6 (Table 4.16) to see the effect of methanol mole fraction. The two
mixtures have different water mole fraction however, it was shown in the previous section that variation of water mole fraction does not significantly affect the phase volume fractions of the hydrocarbon liquid and vapor phases of the mixture and the equation-of-state parameters.

Figures 4.46, 4.47 and 4.48 compare the CCE measurements done on the mixtures with 25 mol% methanol (mixture-6) and 45 mol% methanol (mixture-8) at the above-mentioned temperatures. The addition of methanol increased the aqueous phase volume fractions significantly. The aqueous phase volume fraction increased from about 0.2 to more than 0.65 at all three temperatures. However, this increase in aqueous phase volume fraction is due to combined effect of the increase in mole fraction of water and methanol. The addition of methanol decreased the three phase saturation pressures by approximately 100 psi at all three temperatures.

PR78 Peneloux (T) EOS and PR78 Peneloux (T)-HV EOS were regressed to match the experimentally measured phase volume fractions of mixture-8. Figures 4.43, 4.44 and 4.45 compare the measured phase volume fractions and the calculations using both the equation-of-state models at 200°F, 254°F and 300°F respectively. The same set of binary interaction parameters was used between the components as were used for mixture-6 (given in table 4.18). However, the volume shift parameters were tuned for water and methanol to match the experimental data for mixture-8. The tuned volume shift parameters for water and methanol are given in Table 4.22. An important observation was that the same set of volume shift parameters for water and methanol gave a good fit to the experimental data at all three temperatures. For PR78 Peneloux (T)-HV EOS same set of five interaction parameters between water and methanol were used for mixture-6 (Table 4.15). The result shows that the measured phase volume fractions and equation-of-state calculations show good agreement both qualitatively and quantitatively at 200°F and
254°F. However, at 300°F PR78 Peneloux (T) EOS predicts the hydrocarbon rich phase of the mixture as vapor whereas, PR78 Peneloux (T)-HV EOS predicts it as a liquid phase above the three phase saturation pressure. The exact state of the hydrocarbon rich phase could not be determined as it was a near critical fluid.

Figure 4.49 shows the P-T phase diagram calculated using the above-mentioned equation-of-state models for mixture-8. The figure also compares the measured three phase saturation pressures at 200°F, 254°F and 300°F with the three-phase phase boundary calculated using the EOS models. The result shows good agreement between the measured and calculated values of three phase saturation pressures.

Figures 4.50, 4.51 and 4.52 show the comparison of the phase densities calculated for mixture-8 using the above-mentioned equation-of-state models at 200°F, 254°F and 300°F respectively. The result shows extremely good agreement between the phase densities of all the three phases calculated using the equation-of-state models. Comparing the phase densities calculated for mixture-6 (Figures 4.22, 4.23 and 4.24) and mixture-8 shows that the addition of methanol significantly decreases the aqueous phase density. This significant decrease in aqueous phase density is because the aqueous phase for mixture-8 has much higher methanol molar concentration (Figure 4.53, 4.54 and 4.55) as compared to mixture-6 (Figures 4.25, 4.26 and 4.27). As methanol has lower density than water, it decreases the aqueous phase density for mixture-8. The vapor and hydrocarbon liquid phase densities were not significantly affected by addition of methanol to the mixture.

Figures 4.53, 4.54 and 4.55 show the methanol molar concentration in the three phases calculated for mixture-8 using both the equation-of-state models at 200°F, 254°F and 300°F respectively. The results show that the calculations from both the equation-of-state models agree qualitatively but show some discrepancies quantitatively as were
observed for mixtures-6 and 7. These discrepancies increase with temperature and become significant at 300°F. Comparing the methanol molar concentrations calculated for mixtures 6 and 8 shows that addition of methanol significantly increases the methanol mole fraction in the aqueous phase at all three temperatures.

Figure 4.56 shows the variation of the calculated methanol mole fractions with temperature in the three phases at 1200 psig. The figure compares the methanol mole fraction calculated using both the equation-of-state models. The result shows that the methanol mole fraction in all three phases calculated using PR78 Peneloux (T) EOS vary approximately linearly with temperature, except in hydrocarbon liquid phase which shows some deviation from linear relation. However, those calculated using PR78 Peneloux (T)-HV EOS show large deviation, especially in the hydrocarbon liquid phase, from a linear relation. The analysis suggests that the compositional analysis form PR78 Peneloux (T) EOS, i.e. using classical mixing rules between all the components is more accurate. This analysis is in agreement with that obtained in the previous section.

During the early period of methanol treatment to treat condensate blockage, the cores and the near wellbore region can have a very high molar concentration of methanol. Experiments were thus performed to study the effect of high methanol mole fraction on the phase behavior of hydrocarbon-water-methanol mixtures. A new mixture, mixture-9, was designed to study the effect of very high mole fraction of methanol on the phase behavior of hydrocarbon-water-methanol mixtures. The mixture has 60 mol% methanol, 25 mol% water and 15 mol% of gas mixture-2. Table 4.23 gives the composition of mixture-9. CCE measurements were done on the mixture at 200°F, 254°F and 300°F and the experimentally measured phase volume fractions for the mixture at these temperatures are shown in Figures 4.57, 4.58 and 4.59 respectively.
To analyze the effect of high methanol mole fraction on the phase behavior, the CCE measurements for mixture-9 were compared with those from mixtures-6 and 8. Figures 4.60, 4.61 and 4.62 compare the measure phase volume fractions for the three mixtures at 200°F, 254°F and 300°F respectively. The comparison shows that at all three temperatures, the increase in the mole fraction of methanol increased the aqueous phase volume fraction and decreased the three-phase saturation pressure significantly. At 200°F the three-phase saturation pressure decreased by a small amount from 3845 psig to 3730 psig with the increase in methanol molar concentration from 25 mol% to 45 mol%; however, it decreased significantly to 2980 psig with the increase in methanol mole % to 60 mol%. Similar observation was made at 254°F where the three-phase saturation pressure decreased by only a small amount with the increase in methanol mole % from 25 to 45 but then decreased significantly by about 500 psi with the increase in methanol mole % to 60. At 300°F, increase in methanol mole % from 25% and 45% to 60% changed the phase behavior from aqueous-vapor to a single-phase liquid at high pressures and to a two-phase aqueous liquid-vapor instead of three-phase aqueous-liquid hydrocarbon liquid-vapor at lower pressures. The increase in the methanol mole fraction also decreased the saturation pressure by about 400 psi.

4.6 PHASE BEHAVIOR OF HYDROCARBON-WATER-ISOPROPAOL MIXTURES

Isopropanol (IPA) is a better solvent for some oils than methanol. Gatlin (1959) investigated the use of various alcohols to recover oil. He found experimentally that a slug of isopropyl alcohol (IPA) completely displaces both oil and water. Walker (2000) compared the effect of methanol, ethanol and IPA on the phase behavior of gas condensate hydrocarbon mixtures and observed that increasing the molecular weight of the alcohol decreases the critical pressure and shifts the critical point to lower overall
concentrations of alcohol. He also shows that the liquid dropout and dew point increases with the increasing molecular weight of alcohols and that temperature has less effect on the saturation pressure for the higher molecular weight alcohols (IPA) as compared to lower weight alcohols (methanol). However, in his experiments he only studied the effect of low molar concentration of alcohols on gas condensate hydrocarbons.

This section discusses the effect of IPA on the phase behavior of gas condensate hydrocarbons and water mixtures over a range of temperature and IPA molar concentration. Comparison of the effect of methanol and IPA on gas condensate hydrocarbon-water-alcohol mixtures has also been studied.

To investigate the effect of IPA on the phase behavior of gas condensate hydrocarbon and water mixtures, CCE measurements were performed on hydrocarbon-water-IPA mixtures. A new mixture was prepared by adding 25 mol% water and 25 mol% IPA to the gas condensate mixture-2 (Table 4.5). The overall mixture composition (mixture-10) used for these experiments is given in Table 4.24. This composition is analogous to that of mixture-6, with 25mol% methanol replaced by 25mol% IPA. This will help in direct comparison between the effect of methanol and IPA on the phase behavior of gas condensate hydrocarbons and water mixtures.

CCE measurements were performed on mixture-10 at 200°F, 250°F and 300°F, the same temperatures at which hydrocarbon-water-methanol mixtures were studied. Figures 4.63, 4.64 and 4.65 show the experimentally measured phase volume fractions of the above mixtures at the specified temperatures. At 200°F the mixture is Liquid-Liquid above 4333 psig. At 4333 psig, the mixture flashed to the three phases vapor-liquid-aqueous liquid. At 250°F is also liquid-liquid above the three-phase saturation pressure of 4180 psig and at 4180 psig flashes to three phase vapor-liquid-aqueous liquid. At 300°F the mixture exists as a vapor-aqueous liquid above 3741 psig. At 3741 psig the mixture
flashed into three phases vapor-liquid-aqueous. Thus, the hydrocarbon rich phase is a volatile oil at 200°F and 250°F and a gas condensate fluid at 300°F above the three-phase saturation pressure.

Comparing the results with the liquid dropout of the gas condensate mixture-2 (Figures 4.4, 4.5 and 4.6) shows that adding IPA and water to the mixture increases the saturation pressures at all three temperatures. At 250°F IPA changes the gas condensate hydrocarbons to a volatile oil. It was discussed in section 4.3 that water does not affect the phase behavior of hydrocarbon mixtures significantly, so the effects observed here are primarily due to the addition of IPA.

Figures 4.66, 4.67 and 4.68 show the comparison of the effect of same mole fraction (25 mol% of total mixture) of methanol and IPA on the phase behavior of hydrocarbon-water mixtures. The results show a significant difference in the phase behavior of hydrocarbon-water mixture with the two alcohols. The most significant difference is the reduction of the aqueous phase volume fraction with IPA compared to that with same mole fraction of methanol at all the three studied temperatures. The aqueous phase volume fraction measured for mixture-6 at 200°F, 250°F and 300°F is approximately twice the aqueous phase volume fraction measured for mixture-10. The results show that unlike methanol, IPA prefers the hydrocarbon phase to the aqueous phase. Comparing the aqueous phase volume fraction of the hydrocarbon-water-IPA mixture at 300°F with that of mixture-5 (Figure 4.14) shows that the ratio of the aqueous phase volume fractions for the two is approximately equivalent to the ratio of the water mole fraction in the two mixtures. This suggest that very small fraction of IPA goes to the aqueous phase. Another significant observation was that despite decreasing the aqueous phase volume fraction, IPA increases the total liquid volume fraction i.e. it increases the hydrocarbon liquid (oil phase) volume fraction compared to methanol. Thus, IPA prefers
the liquid hydrocarbon phase compared to the vapor phase. The lower mole fraction of IPA in the vapor phase compared to that of methanol is due to its lower $k$ value than methanol at the same conditions. The vapor pressure calculated using Gomez-Thodos method for methanol at 300°F is 196.33 psia compared to 118.97 psia for IPA (Marker 2001). Thus, due to its lower vapor pressure IPA would prefer the liquid phase to the vapor pressure. This is a favorable effect, as it will result in more residence time for IPA than methanol in cores and reservoir due to less stripping of IPA by the equilibrium gas phase. Also, more hydrocarbon liquid phase volume would result in higher hydrocarbon liquid saturation, which would increase its relative permeability.

4.6.1 Effect of IPA Mole Fraction on the Phase Behavior of Hydrocarbon-Water-IPA Mixtures:

To study the effect of IPA mole fraction on the phase behavior a new mixture with 45 mol% IPA was prepared. The overall mixture composition of the new mixture, mixture-11, is given in Table 4.25. CCE measurements were performed on the mixture at 200°F, 254°F and 300°F. Figures 4.69, 4.70 and 4.71 show the measured phase volume fractions for the mixture at 200°F, 254°F and 300°F respectively. The result shows that at all the three studied temperatures the mixture exists as a single phase liquid at high pressures. At the saturation pressure, the mixture flashes into two phases and no third phase was observed for the studied pressure range. Comparing the phase volume fractions for mixture-11 with those of mixture-8 (Figures 4.43, 4.44 and 4.45) at 200°F, 254°F and 300°F shows that 45 mol% of IPA and methanol has significantly different effect on the hydrocarbon-water mixture phase behavior. The mixture with methanol has two phases at high pressures and forms three phases at lower pressures phases. Whereas, IPA forms a single-phase mixture with hydrocarbon and water at high pressures and form only two phases at lower pressures.
Figure 4.72 compares the effect of temperature on the phase behavior of mixture-11. The results of the CCE measurement done on the mixture at 200°F, 250°F and 300°F show that the temperature in the studied zone has negligible effect on its phase behavior. The increase in temperature only slightly decreased the measured saturation pressure (bubble point pressure) for the mixture, however no effect on the phase volume fractions was observed.

4.7 PHASE BEHAVIOR OF HYDROCARBON- FC 4432 SURFACTANT SOLUTION

Fluorosurfactant FC4432 is a non-ionic polymeric fluorochemical surfactant manufactured by 3M. 2% by weight surfactant solution was prepared in methanol and water (4% by weight). Figure 4.73 gives the structure of the fluorosurfactant FC4432. The composition of the surfactant solution is given in Table 4.26. Coreflood experiments were done with this surfactant solution by Kumar et al. (2005) to treat the damage caused by condensate accumulation. Kumar observed improvements in oil and gas relative permeability that may be due to changes in wettability caused by the reaction of the surfactant with the rock surface.

Phase behavior experiments were done to analyze the effect of surfactant solution on the phase behavior of gas condensate hydrocarbon mixture. To study the effect of surfactant solution on the phase behavior, a mixture was prepared with 50 mol% of surfactant solution and 50 mol% of gas mixture-1. The overall composition of the mixture, mixture-12, is given in Table 4.27. The mixture was pressurized to 1200 psig at 145 °F and left for 1 day to equilibrate in the PVT cell. The experimental pressure and temperature corresponds to the coreflood conditions. The results showed that mixture formed three-phases - vapor, hydrocarbon liquid and a thin second liquid film over the hydrocarbon liquid, at the experimental condition. For the mixture without surfactant and
the same composition of all the other components, only two phases were observed at the above conditions. Thus the result suggests that adding surfactant to the mixture pulls some components from the liquid and/or vapor phase to the vapor-liquid interface. The results of the experiment are given in Table 4.28. Volume of the thin liquid layer was measured and was found to be approximately equal to the combined volume of the surfactant and water. This suggests that surfactant attached itself to water and separated it from the liquid phase to form a thin second liquid film.

To investigate this hypothesis, 2 cc of water was added to the mixture. The mixture was then left to equilibrate at the experimental conditions for 1 day. The phase volume fractions were measured for the mixture then. The measured phase volume fractions are given in Table 4.29. The result shows that addition of 2 cc of water to the mixture increased the volume of the thin liquid phase by approximately 2 cc. No noticeable change in the volumes of the vapor and other liquid phase were observed. This supports the hypothesis that water component is pulled to the vapor-liquid interface by the surfactant. This also suggests that the surface-active forces are greater than the gravitational forces, which otherwise will pull water downwards due to its higher density than the liquid hydrocarbon and methanol. However, no compositional analysis was done to support this hypothesis and thus no concrete conclusions can be made.

4.8 Phase Behavior of Hydrocarbon-Fluorolink S10 Surfactant Solution

Fluorolink S10 is a fluoro-surfactant manufactured by Solvay Solexis. Figure 4.74 shows the chemical structure of the fluoro-surfactant. It is a per-fluoro polyether with ethoxysilane terminal groups. The surfactant was used by Kumar et al. (2005) to treat sandstone and found to increase both oil and gas relative permeability at steady state two-phase flow of gas and condensate after the treatment.
Phase behavior experiments were done to analyze the effect of surfactant solution on the phase behavior of gas condensate hydrocarbon mixture. To study the effect of surfactant solution on the phase behavior, mixture was prepared with 50mol% of surfactant solution and 50mol% of gas mixture-2. Overall Composition of the mixture, mixture-13, is given in Table 4.30. The surfactant solution was prepared with 2% by weight surfactant S10 in methanol. The author conducted experiments at 145 °F and proposes to use them at high temperatures in future. Behavior of surfactant is strongly dependent on temperature and is especially uncertain at high temperatures. So, the effect of surfactant S10 on the phase behavior of gas condensate hydrocarbon-methanol mixtures was studied at 300°F. CCE measurements were done on the mixture at 300°F. Figure 4.75 shows the measured phase volume fractions for the mixture at 300°F. The mixture is a bubble point fluid with the bubble point of 3728 psig. The more important observation was that clear phases were present without any solid precipitates or unclear interfaces. This implies that at this concentration the surfactant S10 is completely soluble in the liquid phase and will not cause any undesirable precipitates during the surfactant treatment to alter the wettability.

The effect of water on the solubility and phase behavior of surfactant S10 was studied next. 50mol% water was added to mixture-13 to get a new mixture with 25mol% surfactant solution and 25mol% gas condensate hydrocarbon. Total mixture composition of the new mixture, mixture-14, is given in Table 4.31. CCE was then performed on the mixture at 300°F. Figure 4.76 shows the measured phase volume fraction for the mixture at 300°F and its comparison with the measured phase volume fractions for mixture-7. Mixture-7 is same as mixture-14 except that mixture-14 has 2% by weight surfactant S10 solution in methanol compared to pure methanol in mixture-7. The comparison shows that the phase volume fractions for both the mixtures are almost same except a slight
increase in the liquid hydrocarbon phase volume fraction for mixture-14. The reason for this is not clear and could be due to experimental error.

There were few important observations made during the CCE measurements. There was a dark foggy thin layer at the interface of the aqueous-vapor interface at high pressures. Also, something, probably surfactant particles, was observed stuck to the glass tube. At around 3500 psig some particle movement was observed and with the lowering pressure, the thickness of the dark layer at the interface increased. With further lowering of pressure, the dark layer got thinner and finally separated from the aqueous phase interface. These observations suggest that addition of water caused some of the surfactant to precipitate out from the methanol solution as the surfactant itself has a very less solubility in water.

4.8 SUMMARY

Phase behavior studies were done on gas condensate hydrocarbon mixtures at high temperature and high pressures. The effect of water and methanol on the phase behavior of retrograde hydrocarbon mixtures was studied. Water had no significant effect on the phase behavior whereas; methanol had significant effect on the phase behavior of hydrocarbon mixtures. The effect of temperature, water mole fraction and methanol mole fraction was studied for hydrocarbon-water-methanol mixtures. The measured data was used to regress PR78 Peneloux (T) EOS and PR78 Peneloux (T)-HV EOS. Temperature dependent volume shift parameters and binary interaction parameters for methanol-water and methanol-hydrocarbon interactions were found to give good match between the measured data and the equation-of-state calculations.

Phase behavior experiments were also done to study the effect of isopropanol on hydrocarbon-water mixtures. Significant difference in the phase behavior of hydrocarbon-water mixture with methanol and IPA was observed. IPA reduces the
aqueous phase volume fraction however, increases the total liquid volume fraction over the studied temperature range.

The effect of fluorosurfactant FC4432 on gas condensate hydrocarbon-water-methanol mixtures was also studied at 145°F and 1200 psig. An additional liquid phase was formed due to the surfactant. However, to study the effect of surfactant more clearly, compositional analysis of the phases is required along with the phase behavior studies. Effect of fluorosurfactant S10 on the phase behavior of gas condensate-methanol and gas condensate-water-ethanol mixtures was also studied experimentally.
Table 4.1 Overall composition of gas mixture 1.

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>0.785</td>
</tr>
<tr>
<td>n-C4</td>
<td>0.15</td>
</tr>
<tr>
<td>n-C7</td>
<td>0.05</td>
</tr>
<tr>
<td>n-C10</td>
<td>0.015</td>
</tr>
</tbody>
</table>

Table 4.2 Critical properties of the components

<table>
<thead>
<tr>
<th>Component</th>
<th>Molecular weight, MW (gms)</th>
<th>Critical Temperature, Tc (K)</th>
<th>Critical Pressure, Pc (Psia)</th>
<th>Critical Volume, Vc (cc/mol)</th>
<th>Critical compressibility factor, Zc</th>
<th>Accentric Factor, ω</th>
<th>Liquid density at 293K, g/cc</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>16.043</td>
<td>190.600</td>
<td>667.20</td>
<td>99.00</td>
<td>0.0080</td>
<td>0.1930</td>
<td>0.6900</td>
</tr>
<tr>
<td>n-C4</td>
<td>58.124</td>
<td>425.200</td>
<td>551.10</td>
<td>255.00</td>
<td>0.1930</td>
<td>0.3510</td>
<td>0.7338</td>
</tr>
<tr>
<td>n-C7</td>
<td>100.205</td>
<td>540.200</td>
<td>396.79</td>
<td>432.00</td>
<td>0.3510</td>
<td>0.6900</td>
<td>0.7338</td>
</tr>
<tr>
<td>n-C10</td>
<td>142.285</td>
<td>617.600</td>
<td>305.68</td>
<td>603.00</td>
<td>0.4900</td>
<td>0.7338</td>
<td>0.7338</td>
</tr>
<tr>
<td>H2O</td>
<td>18.015</td>
<td>647.300</td>
<td>3203.73</td>
<td>56.00</td>
<td>0.3440</td>
<td>0.9990</td>
<td>0.9990</td>
</tr>
<tr>
<td>Methanol</td>
<td>32.042</td>
<td>512.600</td>
<td>1174.21</td>
<td>99.00</td>
<td>0.5590</td>
<td>0.7970</td>
<td>0.7970</td>
</tr>
<tr>
<td>IPA</td>
<td>60.096</td>
<td>508.3</td>
<td>690.38</td>
<td>220</td>
<td>0.248</td>
<td>0.665</td>
<td>0.786</td>
</tr>
</tbody>
</table>
Table 4.3 Volume shift parameters used at different temperatures for equation-of-state calculations

<table>
<thead>
<tr>
<th>Component</th>
<th>Volume shift parameters (ft³/lb-mol) at</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>152°F</td>
</tr>
<tr>
<td>Methanol</td>
<td>0.121</td>
</tr>
<tr>
<td>C1</td>
<td>-0.083</td>
</tr>
<tr>
<td>n-C4</td>
<td>-0.100</td>
</tr>
<tr>
<td>n-C7</td>
<td>0.041</td>
</tr>
<tr>
<td>n-C10</td>
<td>0.260</td>
</tr>
</tbody>
</table>

Table 4.4 Comparison of the original and tuned composition for mixture-1

<table>
<thead>
<tr>
<th>Component</th>
<th>Original composition in mole fractions</th>
<th>Tuned composition in mole fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>0.785</td>
<td>0.795</td>
</tr>
<tr>
<td>n-C4</td>
<td>0.15</td>
<td>0.146</td>
</tr>
<tr>
<td>n-C7</td>
<td>0.05</td>
<td>0.046</td>
</tr>
<tr>
<td>n-C10</td>
<td>0.015</td>
<td>0.014</td>
</tr>
</tbody>
</table>

Table 4.5 Overall composition of gas mixture 2

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>0.081</td>
</tr>
<tr>
<td>n-C4</td>
<td>0.05</td>
</tr>
<tr>
<td>n-C7</td>
<td>0.06</td>
</tr>
<tr>
<td>n-C10</td>
<td>0.08</td>
</tr>
</tbody>
</table>
Table 4.6 Binary interaction parameters used between hydrocarbon components at 200°F

<table>
<thead>
<tr>
<th></th>
<th>C1</th>
<th>n-C4</th>
<th>n-C7</th>
<th>n-C10</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>n-C4</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>n-C7</td>
<td>0.0375</td>
<td>0.0075</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>n-C10</td>
<td>0.0375</td>
<td>0.0075</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 4.7 Binary interaction parameters used between hydrocarbon components at 251.5°F

<table>
<thead>
<tr>
<th></th>
<th>C1</th>
<th>n-C4</th>
<th>n-C7</th>
<th>n-C10</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>n-C4</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>n-C7</td>
<td>0.02875</td>
<td>0.0075</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>n-C10</td>
<td>0.02875</td>
<td>0.0075</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 4.8 Binary interaction parameters used between hydrocarbon components at 300°F

<table>
<thead>
<tr>
<th></th>
<th>C1</th>
<th>n-C4</th>
<th>n-C7</th>
<th>n-C10</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>n-C4</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>n-C7</td>
<td>0.02</td>
<td>0.0075</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>n-C10</td>
<td>0.02</td>
<td>0.0075</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
Table 4.9 Overall composition of mixture 3

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>0.1667</td>
</tr>
<tr>
<td>C1</td>
<td>0.6625</td>
</tr>
<tr>
<td>n-C4</td>
<td>0.1216</td>
</tr>
<tr>
<td>n-C7</td>
<td>0.0375</td>
</tr>
<tr>
<td>n-C10</td>
<td>0.0167</td>
</tr>
</tbody>
</table>

Table 4.10 Variation of binary interaction parameters between methanol and hydrocarbons with temperature

<table>
<thead>
<tr>
<th>Component</th>
<th>Temperature (F)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>152°F</td>
</tr>
<tr>
<td>C1</td>
<td>-0.059</td>
</tr>
<tr>
<td>n-C4</td>
<td>0.222</td>
</tr>
<tr>
<td>n-C7</td>
<td>-0.085</td>
</tr>
<tr>
<td>n-C10</td>
<td>-0.085</td>
</tr>
</tbody>
</table>
Table 4.11 Overall composition of mixture 4

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>0.3643</td>
</tr>
<tr>
<td>C1</td>
<td>0.51605</td>
</tr>
<tr>
<td>n-C4</td>
<td>0.02969</td>
</tr>
<tr>
<td>n-C7</td>
<td>0.03935</td>
</tr>
<tr>
<td>n-C10</td>
<td>0.05247</td>
</tr>
</tbody>
</table>

Table 4.12 Binary interaction parameters between hydrocarbons and water and the volume shift parameters used for the EOS calculations

<table>
<thead>
<tr>
<th>Component</th>
<th>Binary interaction parameter (Kij) with H₂O</th>
<th>Volume shift parameter ft³/lb-mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>0</td>
<td>0.1</td>
</tr>
<tr>
<td>C1</td>
<td>0.55</td>
<td>-0.0833</td>
</tr>
<tr>
<td>n-C4</td>
<td>0.52</td>
<td>-0.1</td>
</tr>
<tr>
<td>n-C7</td>
<td>0.55</td>
<td>0.0405</td>
</tr>
<tr>
<td>n-C10</td>
<td>0.55</td>
<td>0.26</td>
</tr>
</tbody>
</table>
Table 4.13 Overall composition of mixture 5

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fractions</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃OH</td>
<td>0.25</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.2718</td>
</tr>
<tr>
<td>C1</td>
<td>0.387</td>
</tr>
<tr>
<td>n-C4</td>
<td>0.0223</td>
</tr>
<tr>
<td>n-C7</td>
<td>0.0295</td>
</tr>
<tr>
<td>n-C10</td>
<td>0.03935</td>
</tr>
</tbody>
</table>

Table 4.14 Binary interaction parameters between hydrocarbons and water and methanol and the volume shift parameters used for the EOS calculations

<table>
<thead>
<tr>
<th>Component</th>
<th>Binary interaction parameter (Kij) with H₂O</th>
<th>Binary interaction parameter (Kij) with CH₃OH</th>
<th>Volume shift parameter ft³/lb-mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>0</td>
<td>-0.275</td>
<td>0.057</td>
</tr>
<tr>
<td>CH₃OH</td>
<td>-0.275</td>
<td>0</td>
<td>0.139</td>
</tr>
<tr>
<td>C1</td>
<td>0.55</td>
<td>0.29</td>
<td>-0.083</td>
</tr>
<tr>
<td>n-C4</td>
<td>0.52</td>
<td>0.25</td>
<td>-0.100</td>
</tr>
<tr>
<td>n-C7</td>
<td>0.55</td>
<td>0.075</td>
<td>0.0405</td>
</tr>
<tr>
<td>n-C10</td>
<td>0.55</td>
<td>0.075</td>
<td>0.26</td>
</tr>
</tbody>
</table>
Table 4.15 Mixing rules used between components in PR78 Peneloux (T)-HV EOS

<table>
<thead>
<tr>
<th></th>
<th>H₂O</th>
<th>CH₃OH</th>
<th>C₁</th>
<th>n-C₄</th>
<th>n-C₇</th>
<th>n-C₁₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₃OH</td>
<td>Huron-Vidal</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₁</td>
<td>Classic</td>
<td></td>
<td>Classic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-C₄</td>
<td>Classic</td>
<td>Classic</td>
<td>Classic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-C₇</td>
<td>Classic</td>
<td>Classic</td>
<td>Classic</td>
<td>Classic</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-C₁₀</td>
<td>Classic</td>
<td>Classic</td>
<td>Classic</td>
<td>Classic</td>
<td>Classic</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.16 Interaction parameters for Huron-Vidal mixing rules used between water and methanol in PR78 Peneloux (T)-HV EOS

<table>
<thead>
<tr>
<th>Interaction parameters between H₂O and CH₃OH</th>
<th>aij</th>
<th>gij</th>
<th>gji</th>
<th>gij (T)</th>
<th>gji (T)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.2085</td>
<td>-117.73</td>
<td>966.63</td>
<td>-2.84</td>
<td>1.45</td>
</tr>
</tbody>
</table>
Table 4.17 Overall composition of mixture 6

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fractions</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃OH</td>
<td>0.25</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.25</td>
</tr>
<tr>
<td>C₁</td>
<td>0.405</td>
</tr>
<tr>
<td>n-C₄</td>
<td>0.025</td>
</tr>
<tr>
<td>n-C₇</td>
<td>0.03</td>
</tr>
<tr>
<td>n-C₁₀</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Table 4.18 Variation binary interaction parameters used for methanol-water, methanol-hydrocarbon and water-hydrocarbon interactions with temperature

<table>
<thead>
<tr>
<th>Component</th>
<th>200°F</th>
<th>254.5°F</th>
<th>300°F</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Kij with H₂O</td>
<td>Kij with CH₃OH</td>
<td>Kij with H₂O</td>
</tr>
<tr>
<td>H₂O</td>
<td>0</td>
<td>-0.125</td>
<td>0</td>
</tr>
<tr>
<td>CH₃OH</td>
<td>-0.125</td>
<td>0</td>
<td>-0.2</td>
</tr>
<tr>
<td>C₁</td>
<td>0.5</td>
<td>0.5</td>
<td>0.55</td>
</tr>
<tr>
<td>n-C₄</td>
<td>0.52</td>
<td>0.52</td>
<td>0.52</td>
</tr>
<tr>
<td>n-C₇</td>
<td>0.5</td>
<td>0.5</td>
<td>0.55</td>
</tr>
<tr>
<td>n-C₁₀</td>
<td>0.5</td>
<td>0.5</td>
<td>0.55</td>
</tr>
</tbody>
</table>
### Table 4.19 Variation of volume shift parameters with temperature

<table>
<thead>
<tr>
<th>Component</th>
<th>Volume shift parameter (ft(^3)/lb-mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>200(^\circ)F</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.054</td>
</tr>
<tr>
<td>CH₃OH</td>
<td>0.127</td>
</tr>
<tr>
<td>C₁</td>
<td>-0.083</td>
</tr>
<tr>
<td>n-C₄</td>
<td>-0.100</td>
</tr>
<tr>
<td>n-C₇</td>
<td>0.041</td>
</tr>
<tr>
<td>n-C₁₀</td>
<td>0.260</td>
</tr>
</tbody>
</table>

### Table 4.20 Overall composition of mixture 7

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fractions</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>0.50</td>
</tr>
<tr>
<td>CH₃OH</td>
<td>0.25</td>
</tr>
<tr>
<td>C₁</td>
<td>0.2025</td>
</tr>
<tr>
<td>n-C₄</td>
<td>0.0125</td>
</tr>
<tr>
<td>n-C₇</td>
<td>0.015</td>
</tr>
<tr>
<td>n-C₁₀</td>
<td>0.02</td>
</tr>
</tbody>
</table>
### Table 4.21 Overall composition of mixture 8

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fractions</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>0.366667</td>
</tr>
<tr>
<td>CH₃OH</td>
<td>0.45</td>
</tr>
<tr>
<td>C1</td>
<td>0.1485</td>
</tr>
<tr>
<td>n-C4</td>
<td>0.009167</td>
</tr>
<tr>
<td>n-C7</td>
<td>0.011</td>
</tr>
<tr>
<td>n-C10</td>
<td>0.014667</td>
</tr>
</tbody>
</table>

### Table 4.22 Tuned values of volume shift parameters for mixture 8

<table>
<thead>
<tr>
<th>Component</th>
<th>Volume shift parameter (ft³/lb-mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>-0.15</td>
</tr>
<tr>
<td>CH₃OH</td>
<td>-0.053</td>
</tr>
<tr>
<td>C1</td>
<td>-0.083</td>
</tr>
<tr>
<td>n-C4</td>
<td>-0.100</td>
</tr>
<tr>
<td>n-C7</td>
<td>0.041</td>
</tr>
<tr>
<td>n-C10</td>
<td>0.260</td>
</tr>
</tbody>
</table>
Table 4.23 Overall composition of mixture 9

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>0.25</td>
</tr>
<tr>
<td>CH₃OH</td>
<td>0.60</td>
</tr>
<tr>
<td>C1</td>
<td>0.1215</td>
</tr>
<tr>
<td>n-C4</td>
<td>0.0075</td>
</tr>
<tr>
<td>n-C7</td>
<td>0.009</td>
</tr>
<tr>
<td>n-C10</td>
<td>0.012</td>
</tr>
</tbody>
</table>

Table 4.24 Overall composition of mixture 10

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>0.25</td>
</tr>
<tr>
<td>IPA</td>
<td>0.25</td>
</tr>
<tr>
<td>C1</td>
<td>0.405</td>
</tr>
<tr>
<td>n-C4</td>
<td>0.025</td>
</tr>
<tr>
<td>n-C7</td>
<td>0.03</td>
</tr>
<tr>
<td>n-C10</td>
<td>0.04</td>
</tr>
</tbody>
</table>
Table 4.25 Overall composition of mixture 11

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>0.25</td>
</tr>
<tr>
<td>IPA</td>
<td>0.45</td>
</tr>
<tr>
<td>C1</td>
<td>0.243</td>
</tr>
<tr>
<td>n-C4</td>
<td>0.015</td>
</tr>
<tr>
<td>n-C7</td>
<td>0.018</td>
</tr>
<tr>
<td>n-C10</td>
<td>0.024</td>
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</tbody>
</table>

Table 4.26 Surfactant FC4432 solution composition

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>FC 4432 fluorosurfactant</td>
<td>2</td>
</tr>
<tr>
<td>Methanol</td>
<td>94</td>
</tr>
<tr>
<td>Water</td>
<td>4</td>
</tr>
</tbody>
</table>
**Table 4.27 Overall composition of mixture 12**

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surfactant solution</td>
<td>0.50</td>
</tr>
<tr>
<td>C1</td>
<td>0.3925</td>
</tr>
<tr>
<td>n-C4</td>
<td>0.075</td>
</tr>
<tr>
<td>n-C7</td>
<td>0.025</td>
</tr>
<tr>
<td>n-C10</td>
<td>0.0075</td>
</tr>
</tbody>
</table>

**Table 4.28 Phase volumes at 145°F and 1200 psig for the mixture with surfactant.**

<table>
<thead>
<tr>
<th>Equilibrium time (hrs)</th>
<th>Vl1/Vt</th>
<th>VL2/Vt</th>
<th>VL/Vt</th>
<th>Vol L1 (ml)</th>
<th>Vol L2 (ml)</th>
<th>Total Liq vol (ml)</th>
<th>Total mix Vol</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>15.9904</td>
<td>0.668258</td>
<td>16.65871</td>
<td>13.834</td>
<td>0.554</td>
<td>13.279</td>
<td>83.045</td>
</tr>
<tr>
<td>21</td>
<td>15.9788</td>
<td>0.71977</td>
<td>16.69866</td>
<td>13.794</td>
<td>0.594</td>
<td>13.200</td>
<td>82.609</td>
</tr>
</tbody>
</table>

**Table 4.29 Phase volumes at 145°F and 1200 psig after adding 2cc to mixture 12**

<table>
<thead>
<tr>
<th>Equilibrium time (hrs)</th>
<th>Vl1/Vt</th>
<th>VL2/Vt</th>
<th>VL/Vt</th>
<th>Vol L1 (ml)</th>
<th>Vol L2 (ml)</th>
<th>Total Liq vol (ml)</th>
<th>Total mix Vol</th>
</tr>
</thead>
</table>
Table 4.30: Overall composition of mixture 13

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surfactant solution</td>
<td>0.50</td>
</tr>
<tr>
<td>C1</td>
<td>0.405</td>
</tr>
<tr>
<td>n-C4</td>
<td>0.025</td>
</tr>
<tr>
<td>n-C7</td>
<td>0.03</td>
</tr>
<tr>
<td>n-C10</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Table 4.31: Overall composition of mixture-14

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>0.50</td>
</tr>
<tr>
<td>Surfactant solution</td>
<td>0.25</td>
</tr>
<tr>
<td>C1</td>
<td>0.2025</td>
</tr>
<tr>
<td>n-C4</td>
<td>0.0125</td>
</tr>
<tr>
<td>n-C7</td>
<td>0.015</td>
</tr>
<tr>
<td>n-C10</td>
<td>0.02</td>
</tr>
</tbody>
</table>
Figure 4.1: Phase envelope for gas mixture 1.

Figure 4.2 Comparison of the measured liquid dropout for gas mixture-1 with the data from Al-Anazi and calculated using PR78 Peneloux EOS.
Figure 4.3: Phase envelope for gas mixture-2

Figure 4.4: Liquid dropout for gas mixture-2 at 200°F
Figure 4.5: Liquid dropout for gas mixture-2 at 251.5°F

Figure 4.6: Liquid dropout for gas mixture-2 at 300°F
Figure 4.7: Variation of binary interaction coefficients between C1-nC7 and C1-nC10 with temperature.

Figure 4.8: Comparison of liquid dropout for mixture-1 with and without methanol at 152°F
Figure 4.9: Liquid dropout for mixture-3 measured at different temperatures.

Figure 4.10: Variation of binary interaction parameters between methanol and hydrocarbons with temperature.
Figure 4.11: Comparison of phase volume fractions for mixture-4 at 300°F with equation-of-state calculations.

Figure 4.12: P-T phase diagram for mixture-4 calculated using PR78 Peneloux (T) EOS.
Figure 4.13: Water molar concentration in the three phases of mixture-4 at 300°F.

Figure 4.14: Comparison of phase volume fractions for mixture-5 at 300°F with equation-of-state calculations.
Figure 4.15: P-T phase diagram for mixture-5 calculated using PR78 Peneloux (T) EOS.

Figure 4.16: P-T phase diagram for mixture-5 calculated using PR78 Peneloux (T)-HV EOS.
Figure 4.17: Comparison of phase volume fractions for mixture-6 at 200°F with equation-of-state calculations.

Figure 4.18: Comparison of phase volume fractions for mixture-6 at 254.5°F with equation-of-state calculations.
Figure 4.19: Comparison of phase volume fractions for mixture-6 at 300°F with equation-of-state calculations.

Figure 4.20: Variation of binary interaction parameters for methanol-hydrocarbons and methanol-water interactions with temperature.
Figure 4.21: P-T phase diagram for mixture-6 calculated using PR78 Peneloux (T) EOS (referred as classical) and PR78 Peneloux (T)-HV EOS (referred as HV). Also, comparison of measured three-phase saturation pressure with the equation-of-state calculations.
Figure 4.22: Phase densities calculated using PR78 Peneloux (T) EOS and PR78 Peneloux (T)-HV EOS (referred as HV) for mixture-6 at 200°F.

Figure 4.23: Phase densities calculated using PR78 Peneloux (T) EOS (referred as classical) and PR78 Peneloux (T)-HV EOS (referred as HV) for mixture-6 at 254.5°F.
Figure 4.24: Phase densities calculated using PR78 Peneloux (T) EOS (classical) and PR78 Peneloux (T)-HV EOS (HV) for mixture-6 at 300°F

Figure 4.25: Methanol molar concentration calculated using PR78 Peneloux (T) EOS (classical) and PR78 Peneloux (T)-HV EOS (HV) for mixture-6 at 200°F
Figure 4.26: Methanol molar concentration calculated using PR78 Peneloux (T) EOS (classical) and PR78 Peneloux (T)-HV EOS (HV) for mixture-6 at 254.5°F

Figure 4.27: Methanol molar concentration calculated using PR78 Peneloux (T) EOS (classical) and PR78 Peneloux (T)-HV EOS (HV) for mixture-6 at 300°F
Figure 4.28: Comparison of phase volume fractions for mixture-7 at 200°F with equation-of-state calculations.

Figure 4.29: Comparison of phase volume fractions for mixture-7 at 254.5°F with equation-of-state calculations.
Figure 4.30: Comparison of phase volume fractions for mixture-7 at 300°F with equation-of-state calculations.
Figure 4.31: Comparison of measured phase volume fraction for mixture-7 (50 mol% water) and mixture-6 (25 mol% water) at 200 °F. Also, shown the comparison of the measured phase volume fraction data with equation-of-state calculations.
Figure 4.32: Comparison of measured phase volume fraction for mixture-7 (50 mol% water) and mixture-6 (25 mol% water) at 254.5°F. Also, shown the comparison of the measured phase volume fraction data with equation-of-state calculations.
Figure 4.33: Figure 4.32: Comparison of measured phase volume fraction for mixture-7 (50 mol% water) and mixture-6 (25 mol% water) at 300 °F. Also, shown the comparison of the measured phase volume fraction data with equation-of-state calculations.
Figure 4.34: P-T phase diagram for mixture-7 calculated using PR78 Peneloux (T) EOS (referred as classical) and PR78 Peneloux (T)-HV EOS (referred as HV). Also, shown the comparison of measured three-phase saturation pressure with the equation-of-state calculations.
Figure 4.35: The effect of water composition on the phase behavior of hydrocarbon-water-methanol mixtures. Shown is the comparison of P-T phase diagram for mixture-6 (25 mol% water) and mixture-7 (50 mol% water) calculated using PR78 Peneloux (T) EOS.
Figure 4.36: Phase densities calculated using PR78 Peneloux (T) EOS (classical) and PR78 Peneloux (T)-HV EOS (referred as HV) for mixture-7 at 200°F.

Figure 4.37: Phase densities calculated using PR78 Peneloux (T) EOS (classical) and PR78 Peneloux (T)-HV EOS (referred as HV) for mixture-7 at 254.5°F.
Figure 4.38: Phase densities calculated using PR78 Peneloux (T) EOS (classical) and PR78 Peneloux (T)-HV EOS (referred as HV) for mixture-7 at 300°F.

Figure 4.39: Methanol molar concentration calculated using PR78 Peneloux (T) EOS (classical) and PR78 Peneloux (T)-HV EOS (HV) for mixture-7 at 200°F
Figure 4.40: Methanol molar concentration calculated using PR78 Peneloux (T) EOS (classical) and PR78 Peneloux (T)-HV EOS (HV) for mixture-7 at 254.5°F

Figure 4.41: Methanol molar concentration calculated using PR78 Peneloux (T) EOS (classical) and PR78 Peneloux (T)-HV EOS (HV) for mixture-7 at 300°F
Figure 4.42: Variation of methanol molar concentration calculated using PR78 Peneloux (T) EOS (classical) and PR78 Peneloux (T)-HV EOS (HV) at 1200 psig, with temperature for mixture-7.

Figure 4.43: Comparison of measured phase volume fractions for mixture-7 at 200°F with equation-of-state calculations.
Figure 4.44: Comparison of measured phase volume fractions for mixture-7 at 254.5°F with equation-of-state calculations.

Figure 4.45: Comparison of measured phase volume fractions for mixture-7 at 300°F with equation-of-state calculations.
Figure 4.46: Comparison of phase volume fractions for mixture-6 (25 mol% methanol) and mixture-8 (45 mol% methanol) at 200 °F.

Figure 4.47: Comparison of phase volume fractions for mixture-6 (25 mol% methanol) and mixture-8 (45 mol% methanol) at 254.5 °F.
Figure 4.48: Comparison of phase volume fractions for mixture-6 (25 mol% methanol) and mixture-8 (45 mol% methanol) at 300°F.

Figure 4.49: P-T phase diagram for mixture-8 using PR78 Peneloux (T) EOS (classical) and PR78 Peneloux (T)-HV EOS (HV).
Figure 4.50: Phase densities calculated using PR78 Peneloux (T) EOS (classical) and PR78 Peneloux (T)-HV EOS (referred as HV) for mixture-8 at 200°F.

Figure 4.51: Phase densities calculated using PR78 Peneloux (T) EOS (classical) and PR78 Peneloux (T)-HV EOS (referred as HV) for mixture-8 at 254.5°F.
Figure 4.52: Phase densities calculated using PR78 Peneloux (T) EOS (classical) and PR78 Peneloux (T)-HV EOS (referred as HV) for mixture-8 at 300°F.

Figure 4.53: Methanol molar concentration calculated using PR78 Peneloux (T) EOS (classical) and PR78 Peneloux (T)-HV EOS (HV) for mixture-8 at 200°F
Figure 4.54: Methanol molar concentration calculated using PR78 Peneloux (T) EOS (classical) and PR78 Peneloux (T)-HV EOS (HV) for mixture-8 at 254.5°F.

Figure 4.55: Methanol molar concentration calculated using PR78 Peneloux (T) EOS (classical) and PR78 Peneloux (T)-HV EOS (HV) for mixture-8 at 300°F.
Figure 4.56: Variation of methanol molar concentration calculated using PR78 Peneloux (T) EOS (classical) and PR78 Peneloux (T)-HV EOS (HV) at 1200 psig, with temperature for mixture-8.

Figure 4.57: Measured phase volume % for hydrocarbon- water-methanol mixture (mixture-9) at 200°F.
Figure 4.58: Measured phase volume % for hydrocarbon- water-methanol mixture (mixture-9) at 254°F.

Figure 4.59: Measured phase volume fractions for hydrocarbon-water-IPA mixture (mixture-9) at 300°F.
Figure 4.60: Comparison of phase volume fractions for mixture-6, mixture-8 and mixture-9 at 200 °F.

Figure 4.61: Comparison of phase volume fractions for mixture-6, mixture-8 and mixture-9 at 254 °F.
Figure 4.62: Comparison of phase volume fractions for mixture-6, mixture-8 and mixture-9 at 300 °F.

Figure 4.63: Measured phase volume fractions for hydrocarbon-water-IPA mixture (mixture-10) at 200 °F.
Figure 4.64: Measured phase volume fractions for hydrocarbon-water-IPA mixture (mixture-10) at 250°F.

Figure 4.65: Measured phase volume fractions for hydrocarbon-water-IPA mixture (mixture-10) at 300°F.
Figure 4.66: Comparison of phase volume fractions for mixture-6 (with methanol) and mixture-10 (with IPA) at 200 °F.

Figure 4.67: Comparison of phase volume fractions for mixture-6 (with methanol) and mixture-10 (with IPA) at 250 °F.
Figure 4.68: Comparison of phase volume fractions for mixture-6 (with methanol) and mixture-10 (with IPA) at 300°F.

Figure 4.69: Measured phase volume fractions for hydrocarbon-water-IPA mixture (mixture-11) at 200°F.
Figure 4.70: Measured phase volume fractions for hydrocarbon-water-IPA mixture (mixture-11) at 250°F.

Figure 4.71: Measured phase volume fractions for hydrocarbon-water-IPA mixture (mixture-11) at 300°F.
Figure 4.72: Effect of temperature on the phase behavior of mixture-11.

\[ \text{C}_4\text{F}_9—\text{PEG (Polyethylene glycol)} \]

Figure 4.73: Chemical formula for fluoro-surfactant FC4432.

\[ \begin{align*}
  &\text{OCH}_2\text{CH}_3 \\
  \text{(CF}_2\text{CF}_2\text{O})_{14} &\text{Si} \quad \text{OCH}_2\text{CH}_3 \\
  &\text{OCH}_2\text{CH}_3
\end{align*} \]

Figure 4.74: Chemical formula for fluoro-surfactant S10.
Figure 4.75: Measured phase volume fractions for mixture-13 at 300 °F.

Figure 4.76: Comparison of phase volume fractions for mixture-14 (with surfactant) and mixture-7 (without surfactant) at 300 °F.
Chapter 5: Summary, Conclusions and Recommendations

5.1 SUMMARY

A laboratory was setup to perform high-pressure and high-temperature PVT experiments. Constant composition expansion (CCE) measurements were done on hydrocarbon mixtures over a wide range of temperature corresponding to temperatures in gas-condensate reservoirs. Experiments were also performed to study the effect of water and methanol on the phase behavior of hydrocarbons. The effect of various factors including temperature, pressure and composition on the phase behavior of hydrocarbon-water-methanol mixtures was studied. Phase behavior experiments were also conducted on hydrocarbon-water-isopropanol mixtures to investigate the effects of isopropanol on the phase behavior of hydrocarbons. A comparison of the effects of methanol and IPA on the phase behavior of hydrocarbon-water mixtures was also done. Finally, the effect of fluorosurfactants FC4432 and S10 on the phase behavior of gas condensate hydrocarbon-water-methanol mixtures was studied experimentally.

Phase behavior modeling of hydrocarbon mixtures was done using the Peng-Robinson equation-of-state with temperature-dependent Peneloux volume shift correction (PR78 Peneloux (T) EOS). Classical van der Waals mixing rules were used for the hydrocarbon mixtures. The PR78 Peneloux (T) EOS was also used to model hydrocarbon-water-methanol mixtures. The EOS was regressed by tuning the binary interaction parameters and volume shift parameters to match the experimental data. The mixtures were also modeled using Peng-Robinson equation-of-state with temperature dependent Peneloux volume shift correction factors and the Huron-Vidal mixing rules (PR78 Peneloux (T)-HV) and the results of both models are compared. The multi-phase
flash capability of Calsep's PVTSim software was used to calculate phase diagrams for both two and three phase behavior conditions.

5.2 CONCLUSIONS

1. The results show that hydrocarbon mixtures can be modeled accurately using the Peng Robinson equation-of-state with Peneloux volume shift correction and van der Waals mixing rules. The measured equilibrium phase volume fractions were in good agreement with the equation-of-state calculations.

2. Addition of methanol to hydrocarbon mixtures increased the liquid volume fraction and the dew point pressure.

3. Hydrocarbon-methanol mixtures were modeled accurately with PR78 Peneloux (T) EOS by adjusting the binary interaction parameters between each hydrocarbon and methanol. The tuned binary interaction parameters showed a linear dependence on temperature.

4. Water did not have a significant effect on the phase behavior of hydrocarbon mixtures. Although, addition of water caused a third phase to form, the ratio of hydrocarbon liquid volume to vapor phase volume and the dew point pressure remained almost unaffected.

5. PR78 Peneloux (T) EOS was successfully used to model water-hydrocarbon mixtures by tuning the binary interaction parameters between water and hydrocarbons and the volume shift parameter for water.

6. Methanol had a significant effect on the phase behavior of hydrocarbon-water mixtures. Addition of methanol reduced the dew point pressure and increased the aqueous phase volume fraction significantly. This shows that methanol preferred the aqueous phase to the hydrocarbon liquid and vapor phases, even at high temperatures.
7. Hydrocarbon-water-methanol mixtures were modeled accurately using PR78 Peneloux (T) EOS by tuning the binary interaction parameters between methanol and water and methanol and hydrocarbons and the volume shift parameters of methanol.

8. The presence of water significantly affected the interaction between methanol and hydrocarbons. The binary interaction parameters between methanol and each hydrocarbon were different in the presence of water compared to the binary interaction parameters without water.

9. Negative binary interaction parameters between water and methanol, in the temperature range studied, was an important parameter in modeling hydrocarbon-water-methanol mixtures using the PR78 Peneloux (T) EOS.

10. Binary interaction parameters between methanol and water and methanol and each hydrocarbon showed a linear variation with temperature.

11. Temperature-dependent volume shift parameters were extremely important for accurate modeling of hydrocarbon-water-methanol mixtures using PR78 Peneloux (T) EOS. Volume shift parameters of water and methanol were also found to be dependent on the methanol mole fraction.

12. Hydrocarbon-water-methanol mixtures were also modeled accurately using the PR78 Peneloux (T)-HV EOS. Phase behavior and physical property calculations using both equation-of-state models (classical van der Waals and Huron-Vidal mixing rules) were in good agreement, however, the predictions of the phase compositions were different for the two models. Overall there does not seem to be a clear advantage to the more complicated Huron-Vidal mixing rules under the conditions investigated.

13. Isopropanol (IPA) affected the phase behavior of hydrocarbon-water mixtures in a significantly different manner than methanol. Addition of IPA reduced the aqueous phase volume fraction and increased the hydrocarbon liquid phase volume fraction.
14. Fluorosurfactant FC4432 had a significant effect on the phase behavior of hydrocarbon-water-methanol mixtures. The addition of the fluorosurfactant resulted in an additional liquid phase being formed above the liquid hydrocarbon phase. The reason for this additional liquid phase and its composition is not clear.

5.3 Recommendations for Future Work

1. More work is required for phase behavior modeling of hydrocarbon mixtures with high mole fractions of methanol.
2. EOS modeling of hydrocarbon mixtures with water and IPA at high temperatures and pressures has not been done and needs to be studied.
3. Compositional measurements of the phases that form with the hydrocarbon-water-methanol mixtures should be done to better evaluate the EOS models and further calibrate them if necessary.
4. Phase behavior of hydrocarbon-water-methanol mixtures with fluorosurfactant FC4432 is complex and requires some research to analyze and understand its distribution in the different phases.
5. Compositional simulations should be done using the tuned EOS models to understand the complex behavior of the methanol and IPA treatments of high-temperature, high-pressure gas-condensate wells with condensate blocking. Until now neither the experimental data nor the tuned EOS models were available to make such predictions.
Nomenclature

\begin{itemize}
\item \textit{a} \quad \text{energy parameter of PREOS}
\item \textit{a}_{ii} \quad \text{pure component energy parameter}
\item \textit{b} \quad \text{co-volume parameter of PREOS}
\item \textit{b}_i \quad \text{pure component co-volume parameter}
\item \textit{c} \quad \text{Peneloux volume correction}
\item \textit{c'} \quad \text{temperature independent volume correction}
\item \textit{c''} \quad \text{temperature dependent volume correction}
\item \textit{g} \quad \text{energy parameter characteristic for Huron-Vidal mixing rule}
\item \textit{G} \quad \text{Gibbs free energy}
\item \textit{k} \quad \text{binary interaction parameter}
\item \textit{P} \quad \text{pressure (psi)}
\item \textit{P_c} \quad \text{critical pressure (psi)}
\item \textit{R} \quad \text{gas constant}
\item \textit{T} \quad \text{temperature (°F or °R)}
\item \textit{T_c} \quad \text{critical temperature (°R)}
\item \textit{T_{sc}} \quad \text{temperature at standard conditions (°R)}
\item \textit{v} \quad \text{molar volume (ft}^3/\text{lb-mole})
\item \textit{V} \quad \text{volume (cuft)}
\item \textit{V_{ro}} \quad \text{oil relative volume}
\item \textit{x}_i \quad \text{mole fraction of component } i \text{ in oil phase}
\item \textit{y}_i \quad \text{mole fraction of component } i \text{ in gas phase}
\item \textit{Z} \quad \text{compressibility factor}
\item \textit{z}_i \quad \text{overall mole fraction of component } i
\item \textit{Z_{RA}} \quad \text{Racket compressibility factor}
\end{itemize}
References


Li, K. and Firoozabadi, A.: Experimental study of wettability alteration to preferential gas wetting in porous media and its effects,” SPERE (April 2000), 139–149.


Vita

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