RESERVOIR ENGINEERING RESEARCH INSTITUTE

**Wettability Alteration of Porous Media to Gas-Wetting for
Improving Productivity and Injectivity in Gas-Liquid Flows**

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Tom Tang, Erik Santiso, and I were active members of the group working on the US DOE grant DE-FG26-00BC15306 in the first year of the grant. Much progress was made on the experimental aspects. Progress has also been made on the theoretical side.

Chapters I and II provide the results from our extensive experimental work. Chapter III provides a new formulation for the work of cluster formation in single component systems. The continuation of the theory is intended to include work of adhesion for a polymer with various functional groups.

We expect much progress in the second year. A high pressure setup has already been made for reservoir conditions. Theoretical work is also in progress.

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Principal Investigator

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Chapter 1 – Relative Permeability Modification in Gas-Liquid Systems Through Wettability Alteration to Intermediate Gas-Wetting

Guo-Qing Tang and Abbas Firoozabadi

Abstract

The wettability of Berea and chalk samples for gas-oil and gas-water fluids were altered from strong liquid-wetting to intermediate gas-wetting. Two polymers, FC-722 and FC-759, were used to alter the wettability. FC-759 is soluble in water and some 20 times less expensive than FC-722. Gas and liquid relative permeabilities were measured before and after wettability alteration. The results demonstrate a significant increase in liquid-phase relative permeability. Gas-phase relative permeability for a fixed saturation may increase or decrease. However, because of the very high liquid mobility and reduced liquid saturation, the gas mobility also increases for a fixed pressure drop.

A number of liquid injectivity tests were also carried out. The results reveal that the liquid-phase mobility can increase significantly when the wettability of rocks is altered from strong liquid-wetting to intermediate gas-wetting. All the results show clearly that the application of wettability alteration to intermediate gas-wetting may significantly increase deliverability in gas condensate reservoirs.

Introduction

In some gas condensate reservoirs, due to liquid dropout around the wellbore, the well deliverability drops severely¹⁻⁴. Wettability plays an important role in condensate accumulation around the wellbore. The effect of wettability on condensate accumulation in porous media can be explained using the Young-Laplace equation:

$$P_c = \frac{2\mathbf{s} \cos \mathbf{q}}{r} \quad (1)$$

The capillary pressure, P_c , is proportional to interfacial tension, $\mathbf{s}$, and the cosine of the contact angle, $\cos \mathbf{q}$ and is inversely proportional to pore size, r . For a gas-liquid system, strongly liquid-wet porous media can hold high liquid saturation due to the low mobility of wetting phase. Experimental and numerical studies show that the condensate saturation around the wellbore could be reduced by: (1) an increase in viscous forces (also gravity forces)⁵⁻⁶; (2) a decrease in interfacial tension⁷; (3) gas injection⁸; or (4) decrease in liquid wetness⁹. In 1995, Cowney et al.¹⁰ studied the feasibility of improving gas and brine relative permeabilities in Blue Greek coal and Ohio sandstone for a gas-brine-rock system by adding surface-tension reducing agents. They found that it might not be possible to increase gas relative permeability through a lowering of the interfacial tension. Penny et al.¹¹ studied removal of the load water from gas and oil wells through wettability alteration from strong water-wetting to intermediate-wetting. They showed that the load water could easily be removed from either gas or oil wells when the rock was neither oil-wetting nor water-wetting. After wettability alteration, the productivity following

cleanup increased 2 to 3 times. Penny et al. and Cowney et al. did not study the wettability alteration for a gas-oil-rock system.

Recently, Li and Firoozabadi^{6,9} have proposed the enhancement of gas-well deliverability by wettability alteration from strong liquid-wetting to preferential gas-wetting in gas condensate reservoirs. The laboratory study by Li and Firoozabadi⁹ showed that a permanent intermediate gas-wetting could be established in Berea and chalk through chemical treatment.

The major goal of this work is to study the mobility of the gas and liquid phase (both water and hydrocarbon liquids) before and after wettability alteration from strong liquid-wetting to intermediate gas-wetting. For this purpose, in addition to relative permeability measurements, we also conducted various other tests to demonstrate that liquid mobility can be improved significantly due to wettability alteration. Li and Firoozabadi⁹ used the polymer FC-722 in their wettability alteration. This polymer does not dissolve in water and the solvent is expensive. In this work, in addition to FC-722, we used the polymer FC-759 which is soluble in water and is 20 times less expensive than FC-722. This chemical has a specific application in porous media¹².

In this paper, we first present the experimental procedures and the apparatus. Then we discuss the results of (1) the spontaneous imbibition tests without and with initial water saturation; (2) the effect of chemical adsorption on permeability; (3) the gas-oil and gas-water relative permeabilities; (4) the effect of wettability alteration on oil accumulation; and (5) effect of wettability on oil injectivity.

Experimental

Fluids and Rocks. Normal-decane ($n\text{-C}_{10}$) with a specific gravity of 0.73 and a viscosity of 0.92 cp at $T=24^\circ\text{C}$ was used as the oil phase. Distilled water was used to prepare 0.2% (wt.) NaCl brine and was used as the water phase. The specific gravity and viscosity of 0.2% NaCl brine at 24°C were 1.012 and 1.0 cp, respectively. Air was used as the gas phase. The surface tension is 23.4 dynes/cm for air/ $n\text{-C}_{10}$ and about 70 dynes/cm for air/water. Berea sandstone and Kansas chalk were the rock samples. For Berea sandstone, the samples were divided into two groups. The first group of Berea samples had an air permeability of 500 md and a porosity of 21-22%. The second group of Berea samples had an air permeability of 340 md and a porosity of 20%. For Kansas chalk, the air permeability was 1.3-1.5 md and the porosity was about 30-32%. **Table 1** provides permeability, porosity, dimensions, chemical treatment, and other relevant data for Berea and chalk samples used in our work. In this table, B represents Berea sample and C represents chalk sample.

Chemicals. FC-722 and FC-759, manufactured by the 3M corporation, were used to alter the wettability of Berea sandstone and Kansas chalk from strongly liquid-wet to intermediately gas-wet. These two chemicals are the fluoropolymer-type with some specific functional groups. **Fig.1** shows the chemical structure of FC-759. The fluorochemical group provides the water and oil repellency; the silanol and anionic groups chemically bond onto rock surfaces providing a durable treatment; the anionic and nonionic groups make the polymer hydrophilically soluble¹². **Table 2** lists some properties of these two chemicals. FC-722 is colorless, only soluble in a specific fluoro-solvent, and expensive; FC-759 is of a light-yellow color, water-soluble, and less expensive than FC-722. The volatile organic content (VOC) for FC-759 is less than 0.1% and will not cause an environmental problem when applied in the field.

Rock Treatment. A core sample was treated with the chemicals in two different processes:

process-1 and process-2. For process-1, the dry core was saturated with either FC-722 or FC-759 solution after being evacuated for two hours. The core was then aged at room temperature for about 3 days to allow the chemical to adsorb onto the solid surface. After aging, the core was dried by evacuation and then aged at $T=105^{\circ}\text{C}$ for 12 to 24 hours. For process-2, the wet core (containing initial water saturation) was saturated with FC-759 solution and then aged at 90°C for 3 days. After aging, the core was displaced with air to remove liquids. Thereafter, initial water saturation was re-established in the core before it was used for imbibition or coreflooding tests. Process-2 was intended to simulate the application procedure under reservoir conditions.

Spontaneous Imbibition. The core, saturated with air, chemically treated or untreated was placed in either oil or water to perform spontaneous imbibition tests using the setup shown in **Fig.2a**. The core sample was hung under an electronic balance and submerged in a liquid (either oil or brine). Change in weight of the core vs. time was recorded. The decrease in the rate and recovery by spontaneous imbibition of water or oil after chemical treatment give the extent of wettability alteration.

Coreflooding. **Fig.2b** shows a schematic of the apparatus for coreflooding tests, which consisted of a visual coreholder, a pressure transducer, an ISCO pump, an air compressor, a gas pressure regulator, a gas-flow meter, and an electronic balance. The core sample was wrapped in FTP heat-shrinking tubing and placed in a visual coreholder. A confining pressure of 300 psia was used for all tests. The visual coreholder allowed for observation of the movement of liquid/gas interface from the surface of the core. The gas was injected at a constant injection pressure using the gas pressure regulator; the oil (or water) was injected at a constant rate using the ISCO pump. The gas and oil (or water) were mixed in a capillary-tubing mixer before entering the core with two-phase injection. The pressure drop across the core was measured by the pressure transducer. Average oil (or water) saturation in the core was measured vs. time by the electronic balance. Two types of coreflooding tests (1) relative permeability, and (2) oil injectivity, were performed.

Both spontaneous imbibition and coreflooding tests were carried out at room temperature. We are currently conducting tests at reservoir temperature. The results will be published later.

Results

Wettability Alteration at $S_{wi}=0$. In these sets of tests, all the core samples were treated with the chemicals at zero initial water saturation and then used for spontaneous imbibition tests.

Gas-Oil-Berea. **Fig.3** shows oil spontaneous imbibition results for the untreated Berea sample (B-1) and the treated Berea samples (B-2 treated with FC-722, and B-12 treated with FC-759). In order to have a stable intermediate gas-wetting, B-2 was treated with 2% FC-722 twice, but B-12 was treated with 8% FC-759 only once. For the untreated core (B-1), oil imbibed into the core very quickly and all the recoverable gas was produced in less than 60 minutes; the final gas recovery was about 63% (*OGIP*). The imbibition curve for the untreated core shows a strong oil-wetting and was used as a reference to assess the wettability alteration for the treated cores. For the treated cores (B-2 and B-12), the oil imbibition rate was low and final gas recovery was about 9% (*OGIP*) even after the test was carried out for more than 7,000 minutes (5.5 days).

Gas-Water-Berea. Gas recovery by spontaneous water imbibition for the untreated core (B-3) and the treated cores (B-4 and B-13) is presented in **Fig.4**. B-4 and B-13 samples were treated with 2% FC-722 and 8% FC-759, respectively. Similar to the oil imbibition test, water imbibition rate for the untreated core was very high and the final gas recovery was about 58%

(OGIP). For the treated cores (B-4 and B-13), water imbibition was negligible and the final gas recovery was less than 5% (OGIP).

Gas-Oil-Chalk. Fig.5 presents the data of spontaneous oil imbibition for the untreated core (C-1) and the treated cores (C-2 and C-11). C-2 sample was treated with 2% FC-722 and C-11 sample was treated with 5% FC-759 twice. A high rate of oil imbibition was observed for the untreated core (C-1); the final gas recovery was about 65% (OGIP). For the treated cores (C-2 and C-11), the oil imbibition rate decreased significantly; the final gas recovery was less than 6% (OGIP).

Gas-Water-Chalk. Fig.6 shows the data for the spontaneous water imbibition tests using the untreated and treated cores. C-1 sample was the same core previously used for oil imbibition test; C-3 sample was treated with 2% FC-722 and C-13 sample was treated with 8% FC-759. Water imbibition in the treated cores was very slow and the final gas recovery for C-3 sample was about 3% (OGIP) and for C-12 sample was about 8.5% (OGIP). The final recovery for the untreated core (C-1) was about 62% (OGIP).

The results presented in Figs.3-6 demonstrate that wettability of Berea sandstone and Kansas chalk could be altered from strong liquid-wetting (SLW) to intermediate gas-wetting by treatment with either FC-722 or FC-759.

Wettability Alteration with S_{wi} . For these sets of tests, the treatment was made using process-2. The cores saturated with 100% water were displaced with air to remove water to a designated initial water saturation (< 20%). They were then placed into a beaker filled with 8% FC-759 solutions immediately to avoid water evaporation and were saturated with the chemical solution by applying vacuum in a dessicator containing the beaker. The cores were, then, aged at 90°C for 3 days without drying. After aging, air was injected into them at room temperature to remove the solution. The initial water saturation was re-established by saturating the treated cores with water followed by air displacement. The re-established initial water saturation was close to that established initially.

Fig.7a shows the results of spontaneous oil imbibition for B-14, B-16, and B-17 samples. The initial water saturation was zero for B-14, 9.5% for B-16, and 16.2% for B-17. Fig.7a reveals that the initial water saturation did not affect the effectiveness of wettability alteration by FC-759. The oil imbibition rate and the final gas recovery show a decline in imbibition with increase in initial water saturation from zero to 16.2%. Fig.7b depicts the results of spontaneous water imbibition for B-18 and B-19 samples. The initial water saturation was 8.5% for B-18 and 16.5% for B-19. Compared to the spontaneous oil imbibition shown in Fig.7a, the water imbibition rate and the final gas recovery are higher; the final gas recovery was about 15% (OIGP). Increase in initial water saturation did not affect the water imbibition behavior. Similar results were also obtained for chalk samples (see Fig.8). The C-14 sample was treated with 8% FC-759 at zero initial water saturation. The C-15 sample was treated with 8% FC-759 at an initial water saturation of about 12%. The results shown in Fig.8 demonstrate that initial water saturation reduced final gas recovery from 10% to 3% (OGIP) which is in agreement with the results obtained for Berea. The interaction between gas, water, and oil phases may cause such a performance.

Stability Testing. Establishment of stable intermediate gas-wetting is the major goal of our work. We examined the stability of intermediate gas-wetting on treated cores. Fig.9a presents the results for the repeated tests for spontaneous oil imbibition. B5 sample treated with 2% FC-722

was repeatedly used. After each test, the core was dried at 105°C to remove all the oil from the core and weighed to check change in chemical adsorption. The results for the repeated imbibition tests were nearly the same. No chemical desorption was observed; the weight of the dry core after each test remained the same. The results in **Fig.9b** indicate that even after the treated cores (B-6 and C-5) were submerged in oil for more than 90 days, the final gas recovery did not change after 15 days, which indicates a stable altered wettability by the chemicals.

Therefore, one may assume that the adsorption of FC-722 and FC-759 onto the surfaces of the selected rocks is stable and permanent.

Assessment of Wettability Alteration. The results presented above reveal that wettability of Berea and Kansas chalk can be altered significantly by chemical treatment. In order to assess wettability alteration, we used the following equation to estimate a pseudo-contact angle for the treated cores (see the derivation in the **Appendix**).

$$V^2 = \sqrt{\frac{8k}{f}} \frac{SA_e^3 \cos \mathbf{q}_p}{2m} t \quad (2)$$

In the above equation, V is imbibed phase volume, k permeability, f porosity, S interfacial tension, A_e effective section area, m viscosity, $\mathbf{q}_p$ pseudo-contact angle, and t imbibition time.

If we assume that the permeability, porosity, interfacial tension, and viscosity are constant, Eq.2 can be expressed as

$$V^2 = K \cos \mathbf{q}_p t \quad (2a)$$

where K is a constant. Plot of V^2 vs. t gives a straight line when the contact angle is constant in the course of imbibition. One could then estimate a pseudo-contact angle from the slope of the straight line. Using imbibition data of untreated core as a reference, we could estimate the pseudo-contact angle for treated core using

$$\cos \mathbf{q}_{p_1} = \frac{K_1}{K_2} \cos \mathbf{q}_{p_2} \quad (3)$$

In Eq.3, subscripts 1 and 2 refer to treated and untreated core, respectively. Here we assume the pseudo-contact angle for untreated core to be zero. The pseudo-contact angle estimated from Eq.3 for treated Berea and chalk samples are about 90 degrees (see **Table-1**), giving further indication that the rock surfaces were altered to intermediate gas-wetting.

Chemical Adsorption and Effect on Permeability. Permeability reduction due to polymer adsorption onto rock surfaces has been reported in the literatures¹³. In the following, we examined the effect of chemical treatment on permeability.

We determined the chemical adsorption on Berea and chalk samples by weighing dry core before and after chemical treatment. The adsorption of FC-722 on Berea sandstone was about 2.2-2.4 mg per g-sand, and on chalk was about 2.5-2.8 mg per g-chalk; the adsorption of FC-759 on Berea was 5.0-6.1 mg of g-sand and on chalk was about 0.8-1.6 mg of g-chalk (see **Table-1**).

Adsorption of FC-759 on chalk was less than that on Berea. This may be due to negatively-charged chalk surfaces that have some repellency to the anionic groups of FC-759.

Using measured chemical adsorption data, we estimated the thickness of chemical coating on the rock surfaces. The surface areas of the selected rocks were estimated from the permeability and porosity data using the Cozeny correlation¹⁴; the estimated surface area of Berea was about 0.03 m² per g sandstone and of chalk was about 2.73 m² per g-chalk. The average thickness of FC-722 onto Berea surface was about 0.08 μm and onto chalk surface was about 0.002 μm; the average thickness of FC-759 onto Berea surface was 0.09 μm and was about 0.0004 μm onto chalk surface. When a core was treated twice, the chemical film thickness nearly doubled.

The absolute permeability to oil was determined before and after a core was treated with chemicals. B-9 and C-6 samples were untreated; B-10 and C-7 samples were treated with 2% FC-722 twice; and B-11 and C-8 samples were treated with FC-759 twice. Oil permeability was 344 md for untreated Berea and 335 md for treated Berea. Reduction in permeability was negligible for Berea. For the low permeable chalk, oil permeability was 1.32 md for untreated chalk and 1.20 md for treated chalk. Reduction in permeability was less than 10%. Therefore, there is no appreciable reduction in permeability after chemical treatment.

Gas and Oil (Water) Relative Permeabilities. In order to reduce the end effect, core samples with a length of about 18 cm were used. Gas and oil (water) relative permeabilities were measured by the steady-state method. Gas was injected at a constant inlet pressure using a gas pressure regulator. Oil (water) was injected at a constant rate using an ISCO pump. Gas and oil (water) were mixed before entering the core. We assumed that steady-state was established when the oil (water) saturation in the core, gas and oil (water) production rates, and pressure drop were nearly constant. We mainly studied gas and oil (water) relative permeabilities for imbibition. The effect of capillary pressure was neglected due to high flow rate and the use of long core in the tests.

Effect of Wettability on k_{rg} and k_{ro} (k_{rw}). Fig.10 shows measured gas and oil relative permeabilities for untreated core (B-9) and treated cores (B-10 and B-11). B-10 sample was treated with 2% FC-722 twice and B-11 sample was also treated with 5% FC-759 twice. Treatment for these two cores was for $S_{wi}=0$. A duplicate test for each core was made and the results were nearly the same. We only present the results for one of the duplicate tests for each core. A significant effect of wettability alteration on both gas and oil relative permeabilities was observed. After wettability alteration from strong oil-wetting to intermediate gas-wetting (1) the oil saturation at the point for which $k_{rg}=k_{ro}$ reduced from 0.54 to about 0.45 PV, (2) the cross-point relative permeability increased from 0.03 to 0.15 indicating an improvement of two-phase flow mobility, (3) the gas relative permeability decreased and oil relative permeability increased, and (4) the residual oil saturation decreased from 0.42 to about 0.15 PV. These results are in agreement with relative permeabilities in oil-water systems when one alters wettability¹⁵.

Gas and water relative permeabilities were also measured in untreated core (B-9) and treated core (B-10). The effect of wettability alteration on gas and water relative permeabilities shows a trend similar to that for gas and oil relative permeabilities (see Fig.11). Water relative permeability increased significantly at $S_w>0.5$ PV. Residual water saturation decreased from 0.44 to 0.25 PV. Reduction in residual water saturation after chemical treatment was less than residual oil saturation (see Fig.10).

Fig.12 presents gas and oil relative permeabilities for the untreated chalk sample (C-6) and the treated chalk sample (C-7). C-7 sample was treated with 2% FC-722. Due to low permeability,

the gas injection pressure was about 50 psi. It is interesting to note that both gas and oil relative permeabilities increased for $S_o > 0.2$ after wettability alteration to intermediate gas-wetting. Increase in oil relative permeability was greater than that for gas relative permeability. Also, the oil saturation at the cross-point $k_{ro}=k_{rg}$ decreased from 0.57 to 0.45 PV after the wettability alteration; relative permeability at the cross-point increased from 0.035 to 0.12. Residual oil saturation decreased from 0.45 to 0.15 PV.

Oil (or water) saturation at the cross point, $k_{rg}=k_{ro}$, for treated cores was less than 0.5 PV for treated Berea and treated chalk, implying a preferential gas-wetting. This result is in line with the spontaneous imbibition measurements. Figs.10 and 12 imply that the effect of wettability alteration on gas relative permeability may depend on porous media.

Effect of Viscous Forces on k_{rg} and k_{ro} . Gas and oil relative permeabilities measured at pressure gradients of 0.1, 0.2, and 0.3 psi/cm for both untreated (B-9) and treated cores (B-10) are presented in **Figs.13a** and **13b**, respectively. For untreated core, gas relative permeability increased systematically with increase in pressure gradient while oil relative permeability did not change much. This result is in agreement with the experimental results by Henderson et al.¹⁶ and Chen et al.¹⁷ and the modeling results by Li and Firoozabadi⁶. For treated core, both gas and oil relative permeabilities increased with pressure gradient systematically; the increase in k_{rg} at $S_o < 0.5$ PV seems to be small. Similar results were obtained in an intermediate wettability rock for an oil/water system by Heaviside et al.¹⁸ An important observation is that as the pressure gradient increases from 0.1 to 0.3 psi/cm, residual oil saturation decreases from 0.15 PV to 0.04 PV for treated core, but it does not decrease for untreated core (as expected). This result is in agreement with our work on the effect of wettability alteration on oil recovery from low-permeability chalks by water injection¹⁹.

Effect of Initial Water Saturation on k_{rg} and k_{ro} . We assumed the initial water saturation is immobile due to low saturation. **Fig.14a** shows the effect of initial water saturation on gas and oil relative permeabilities for untreated Berea (B-9). Increase in initial water saturation from zero to 0.11 PV did not affect oil relative permeability; it reduced gas relative permeability significantly. Note that oil saturation at $k_{ro}=k_{rg}$ and relative permeability at the cross-point did not change with increase in initial water saturation. The effect of initial water saturation on gas and oil relative permeabilities shows an opposite effect in treated Berea (see **Fig.14b**). Increase in initial water saturation from zero to 0.075 PV did not change gas relative permeability, but reduced oil relative permeability significantly. Oil saturation at $k_{ro}=k_{rg}$ increased from 0.41 to 0.45 PV and relative permeability at the cross-point decreased from 0.18 to 0.12.

In our work, the effect of initial water saturation on gas and oil relative permeabilities for strong liquid-wetting and intermediate gas-wetting for Berea is different from the work of Narahara et al.²⁰. In their work with water-wet and mixed-wet Berea (water-wetting and mixed-wetting in the content of oil and water phases), they did not find any effect of initial water saturation on either gas or oil relative permeability. The effect of initial water saturation on gas and oil relative permeability needs further study.

Reduction in Oil Saturation. Effect of wettability on oil saturation was also studied using the following tests. Gas and oil were first mixed in a capillary-tubing mixer and then injected simultaneously into an air-saturated core. Gas injection pressure was changed from 2 to 6 psi and oil was injected at a rate of 4 cm³/hr. Injected ratio of gas to oil was large and inlet pressure was close to gas injection pressure. Outlet pressure was atmospheric. Average oil saturation in the core increased with injection and no oil was produced from the outlet at early time due to oil

accumulation in the core. The oil breakthrough time in untreated core was much greater than that in treated core. In the tests with untreated core (B-9), there was an interface between the invaded-oil phase and displaced-gas phase; the interface moved toward the outlet with time and the displacement was piston-like. Oil broke through from the core outlet at oil saturation of around 0.63 PV for the test at a pressure gradient of 0.1 psi/cm (see **Fig.15a**). Thereafter, oil was produced continuously and average oil saturation in the core was nearly constant. Increase in pressure gradient from 0.1 to 0.3 psi/cm resulted in a decrease in average oil saturation from 0.65 PV to 0.53 PV in untreated core.

With treated core (B-10), we did not observe an interface between invaded-oil phase and displaced-gas phase. Oil broke through from the core at an oil saturation of 0.25 PV for the test at a pressure gradient of 0.1 psi/cm. Thereafter, oil saturation increased to 0.3 PV. Oil accumulation was more sensitive to pressure gradient for treated core. It decreased from 0.3 to 0.12 PV as pressure gradient increased from 0.1 to 0.3 psi/cm (see **Fig.15b**), indicating substantial increase in oil mobility with altered wettability.

As oil saturation decreased from about 0.55 to 0.15 PV due to wettability alteration from strong liquid-wetting to intermediate gas-wetting (see Fig.15), gas relative permeability increased from 0.05 to 0.5 due to reduced oil saturation (see Fig.10). These results imply that gas-well deliverability may increase substantially when wettability is altered to intermediate gas-wetting.

Increase in Oil Injectivity. The setup in **Fig.16** was used to make another comparison of two-phase gas-liquid flow with and without wettability alteration. Untreated and treated cores were assembled in parallel. The difference in oil injectivity from these two cores could be attributed to the sole effect of the wettability.

Oil was injected at a constant rate (for Berea the rate was 4 cm³/min and for chalk it was 0.33 cm³/min). Oil production rate from the outlet of each core was measured separately after breakthrough. Before oil breakthrough, oil rates of the individual cores at the inlet was calculated from gas production rates using material balance. The test was initiated with 100% gas saturated cores.

Figs. 17 shows the results for oil injectivity in Berea. The pressure drop quickly increased to about 7 psi, then decreased gradually to about 6 psi. Oil injection rate at the inlet of the untreated core varied from 0.5 to 0.9 cm³/min, but at the inlet of the treated core varied from 3.0 to 3.5 cm³/min. The ratio of oil injectivity in treated Berea and in untreated Berea was about 4 to 6. Oil injectivity data for chalk are shown in **Fig.18**. The pressure drop after breakthrough was about 43 psi. Oil injection rate in the treated core increased quickly and then gradually stabilized at about 0.28 cm³/min; oil injection rate in untreated core was initially higher due to strong effect of capillary pressure, but it decreased quickly and then gradually stabilized at about 0.05 cm³/min. The ratio of oil injectivity in treated core to untreated core was about 6.

This above simple tests firmly establish the benefit of wettability alteration for the increase in oil mobility in two-phase gas-liquid flow.

Discussion and Concluding Remarks

The work presented in this paper and the work in Refs. 6 and 9 have established that in gas-oil systems, the wettability of porous rocks can be altered to intermediate gas-wetting. In this work, we have demonstrated that as a consequence of intermediate gas-wetting, liquid phase mobility increases significantly. One application of wettability alteration to intermediate gas-wetting is

enhancement of well deliverability in the gas condensate reservoirs that have experienced sharp drop in deliverability due to condensate dropout around the wellbore. In order to proceed with field application, the research work should advance along two main directions. In one direction, the effect of high temperature on wettability alteration to intermediate gas-wetting should be studied. In another direction, the search of other suitable polymers should continue. We have embarked upon the work on both directions; in future publications the results will be made available.

Nomenclature

A_e = effective sectional area, cm^2
 C_{ad} = chemical adsorption, mg/g-rock
 L = length, cm
 K = coefficient, dimensionless
 k = permeability, md
 k_r = relative permeability, fraction
 $OGIP$ = original gas in place, %
 Δp = pressure drop, psi
 P_c = capillary pressure, psi
 PV = pore volume, cm^3
 q_o = oil injection rate, cm^3/min
 SLW = strong liquid-wetting
 S_{wi} = initial water saturation, fraction of PV
 t = time, min or day

Greek Letter

f = porosity, fraction
 μ = viscosity, cp
 θ = contact angle, degree
 σ = interfacial tension, dyne/cm

Subscripts

g = gas
 o = oil
 w = water

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Table-1 Core Properties and Chemical Treatment Data							
Core	k md	f %	L cm	S_{wi} PV	Chem. Treatment	C_{ad} mg/g -rock	ϕ_p deg.
B-1	507	21.5	6.05	0	no	0	0
B-2 ^b	522	21.9	6.1	0	2% FC-722	4.6	90
B-3	511	22.1	6.2	0	no	0	0
B-4	503	22.2	6.0	0	2% FC-722	2.4	90
B-5	495	21.7	6.3	0	2% FC-722	2.2	90
B-6	552	21.7	5.5	0	8% FC-759	6.0	90
B-9	341	20.1	18	0	no	0	0
B-10 ^b	343	20.0	17.9	0	2% FC-722	4.5	-
B-11 ^b	339	20.1	18.0	0	5% FC-759	10.3	-
B-12	501	22.1	6.3	0	8% FC-759	6.1	90
B-13	489	22.0	6.5	0	8% FC-759	6.0	90
B-14	513	21.9	6.2	0	8% FC-759	5.9	90
B-15 ^a	487	20.9	6.1	9.8	8% FC-759	5.7	-
B-16 ^a	495	21.3	5.9	16.2	8% FC-759	5.0	-
B-17 ^a	503	21.5	6.3	8.5	8% FC-759	6.3	-
B-18 ^a	483	20.5	6.8	16.5	8% FC-759	5.2	-
C-1	1.34	31.1	5.6	0	no	0	0
C-2	1.32	32.0	5.9	0	2% FC-722	2.5	90
C-3	1.30	31.7	5.7	0	2% FC-722	2.8	90
C-5	1.34	32.0	5.5	0	8% FC-759	0.9	90
C-6	1.33	31.8	18.1	0	no	0	0
C-7	1.31	32.2	18.0	0	2% FC-722	2.7	90
C-8	1.28	32.0	17.9	0	8% FC-759	1.0	-
C-11 ^b	1.33	32.0	5.9	0	5% FC-759	1.6	-
C-12 ^b	1.33	32.1	6.1	0	5% FC-759	1.4	-
C-14	1.28	31.6	5.8	0	8% FC-759	0.8	90
C-15	1.30	31.9	5.5	11.7	8% FC-759	0.9	-

Diameter of the core was 2.54 cm for Berea and 2.2 cm for chalk.

^a core was aged with S_{wi} at $T=90^\circ\text{C}$ without drying

^b core was treated twice

Table-2 Properties of Chemicals		
Chemical	FC-722	FC-759
MW	10 ³	10 ³
Concentration, %	2	5-8
Viscosity, cp at 25°C	1	3.3
Specific gravity	1.8	1.1
Boiling point, °C	59	100
Color	clear	light-yellow
VOC, %	-	<0.1

Appendix: Expression for Pseudo-Contact Angle

For a capillary tube with a diameter of r , capillary pressure, P_c , between air and invading liquid can be expressed as:

$$P_c = \frac{2\mathbf{s} \cos \mathbf{q}}{r} \quad (\text{A-1})$$

where $\mathbf{s}$ is interfacial tension between air and invading liquid, and $\mathbf{q}$ is the liquid-solid-air contact angle. Using the Poiseuille equation, liquid flow rate in a capillary tubing can be expressed as:

$$q = \frac{\mathbf{r}^4 \Delta p}{8\mathbf{m}l} \quad (\text{A-2})$$

where q is liquid flow rate, l length, and Δp pressure drop across the tube. For spontaneous imbibition, capillary force is the only force driving liquid into the tube when gravity is negligible. Therefore, $P_c = \Delta p$. Substituting Eq.A-1 into Eq.A-2, advancing liquid rate in the tube can be expressed as:

$$q = \frac{dl}{dt} = \frac{\mathbf{r}^3 \mathbf{s} \cos \mathbf{q}}{4\mathbf{m}l} \quad (\text{A-3})$$

Assuming $l=0$ at $t=0$ and integrating Eq.A-3 with respect to l gives the expression for calculating the distance of liquid advancing in the capillary tube at time t :

$$l^2 = \frac{\mathbf{r}^3 \mathbf{s} \cos \mathbf{q}}{2\mathbf{m}} t \quad (\text{A-4})$$

Let A denote the cross-section area of the tube and V the liquid volume at time t , then $l=V/A$, Substituting $l=V/A$ into Eq.A-4, the volume of the advancing liquid into the pore space of the tube is given by:

$$V^2 = \frac{\mathbf{s} \mathbf{r} A^3 \cos \mathbf{q}}{2\mathbf{m}} t \quad (\text{A-5})$$

Eq.A-5 shows that a plot of V^2 vs. t would give a straight line provided the interfacial tension between liquid and air, the viscosity of liquid, and contact angle do not change with time. The slope of the straight line can provide the contact angle from Eq.A-5. For porous media, we use an effective cross-section area of the rock, A_e , instead of A and set $r = \sqrt{8k/\mathbf{f}}$ in Eq.A-5. Using Eq.A-5, the liquid volume imbibed into the pore space at time t can be expressed as:

$$V^2 = \sqrt{\frac{8k}{\mathbf{f}}} \frac{\mathbf{SA}_e^3 \cos \mathbf{q}_p}{2\mathbf{m}} t \quad (\text{A-6})$$

Note that $\mathbf{q}_p$ is the pseudo-contact angle in porous media.

R_f-Fluorochemical, A -Anionic group, N -Nonionic group, W≠X≠Y≠Z

Fig.1–Chemical Structure of FC-759 (Ref.12)

Fig.2–Schematic of the Apparatus for Imbibition and Coreflooding

Fig.3-Gas Recovery by Spontaneous Oil Imbibition for Treated and Untreated Berea

Fig.4-Gas Recovery by Spontaneous Water Imbibition for Treated and Untreated Berea

Fig.5-Gas Recovery by Spontaneous Oil Imbibition for Treated and Untreated Chalk

Fig.6–Gas Recovery by Spontaneous Water Imbibition for Treated and Untreated Chalk

(a) Spontaneous Oil Imbibition

(b) Spontaneous Water Imbibition

Fig.7–Effect of S_{wi} on Wettability Alteration of Berea by 8% FC-759

Fig.8—Effect of S_{wi} on Wettability Alteration of Chalk by 8% FC-759: Spontaneous Oil Imbibition

(a) Repeated Spontaneous Oil Imbibition

(b) Long-Term Spontaneous Oil Imbibition

Fig.9—Stability Testing for Treated Berea and Chalk

Fig.10—Gas and Oil Relative Permeabilities for Treated and Untreated Berea

Fig.11—Gas and Water Relative Permeabilities for Treated and Untreated Berea

Fig.12—Gas and Oil Relative Permeabilities for Treated and Untreated Chalk

(a) Untreated Berea: B-9

(b) Treated Berea: B-10

Fig.13—Effect of Viscous Forces on Gas and Oil Relative Permeabilities for Treated and Untreated Berea with 2% FC-722

(a) Untreated Berea: B-9

Fig.14—Effect of S_{wi} on Gas and Oil Relative Permeabilities for Treated and Untreated Berea

Fig.15—Effect of Viscous Forces on Oil Accumulation for Treated and Untreated Berea

Fig.16–Schematic of Oil Injectivity Tests

Fig.17–Effect of Wettability on Oil Injectivity in Treated and Untreated Berea

Fig.18–Effect of Wettability on Oil Injectivity in Treated and Untreated Chalk

Chapter 2 – Wettability Alteration to Intermediate Gas-Wetting in Porous Media at Elevated Temperatures

Tom Tang and Abbas Firoozabadi

Abstract

Wettability alteration to intermediate gas-wetting in porous media by treatment with FC-759, a fluoropolymer surfactant, has been studied experimentally. Berea sandstone was used as the main rock sample in our work and its wettability before and after chemical treatment was studied at various temperatures from 25 to 93°C. We also studied recovery performance for both gas/oil and oil/water systems for Berea sandstone before and after wettability alteration by chemical treatment.

Our experimental study showed that chemical treatment with FC-759 can result in: (1) wettability alteration from strong liquid-wetting to stable intermediate gas-wetting at room temperature and at elevated temperatures; (2) neutral wetting for gas, oil, and water phases in two-phase flow; (3) significant increase in oil mobility for gas/oil system; and (4) improved recovery behavior for both gas/oil and oil/water systems.

This work reveals a potential for field application for improved gas-well deliverability and well injectivity by altering the rock wettability around wellbore in gas condensate reservoirs from strong liquid-wetting to intermediate gas-wetting.

Introduction

Wettability alteration in water-oil systems and its effect on oil recovery performance have been studied extensively in the past several decades⁽¹⁻¹⁰⁾. However, wettability alteration in gas-liquid systems (that is, gas-oil and gas-water) through chemical treatment has only been studied recently. Li and Firoozabadi⁽¹¹⁾ and Tang and Firoozabadi⁽¹²⁾ investigated wettability alteration from strong liquid-wetting to intermediate gas-wetting using fluorochemical polymer surfactants, FC-722 and FC-759. They showed that a stable intermediate gas-wetting can be established in Berea sandstone and chalk at room temperature. Through wettability alteration, the liquid-phase mobility for a gas-liquid system increases significantly, showing potential to improve gas well deliverability in gas condensate reservoirs. In references 11 and 12, the wettability alteration in intermediate gas-wetting has been studied at room temperature. One major goal of this work is the study of the effect of wettability alteration at high temperatures which are encountered in gas reservoirs. In this work, we will first present the experimental and the chemical treatment process, followed by imbibition and coreflooding tests.

Experimental

Fluids and Rocks

Normal decane ($n\text{-C}_{10}$) with specific gravity of 0.73 at $T=25^\circ\text{C}$ was used as the oil phase in most experiments. In some tests, we used normal tetradecane ($n\text{-C}_{14}$). The measured viscosity of $n\text{-C}_{10}$ was 0.92 cp at $T=25^\circ\text{C}$ and 0.51 cp at $T=90^\circ\text{C}$. In the presentation of results, when we use the term oil, it means that $n\text{-C}_{10}$ is used in the tests. Distilled water dissolved with 0.2% NaCl (brine) was used as the water phase. The specific gravity of brine was 1.012. The viscosity of brine was 1.012 cp at $T=25^\circ\text{C}$ and 0.54 cp at $T=90^\circ\text{C}$. Air was used as the gas

phase. Berea sandstone with air permeability of 320 md and a porosity of 20% was used in most experiments. Two dimensions of Berea were used in this work. One had a length of about 5-6 cm and a diameter of 2.54 cm; this group was mainly used for spontaneous imbibition tests. The other one had a length of 18 cm and a diameter of 2.54 cm; this group was mainly used for core flooding tests. Kansas outcrop chalk with an air permeability of 1.5 md and a porosity of 32% was used in some experiments for the purpose of examining the results for a second rock type. The length of chalk samples was about 6-7 cm and diameter was 2.54 cm. Relevant data of the rock properties are listed in Table 1.

Chemical Treatment

FC-759 and FC-722, manufactured by 3M Specialty Materials were used to alter the wettability of Berea and chalk samples from strongly liquid-wetting to intermediate gas-wetting. These chemicals have the specific functional groups which serve different purposes. Among these chemicals, FC-759 was used for most of this study because it was developed for coating on the surface of porous media⁽¹³⁾. Figure 1 shows the chemical structure of FC-759. The fluorochemical group provides water and oil repellency; the silanol and anionic groups chemically bond onto the rock surfaces providing a durable treatment; the anionic and nonionic groups make the polymer hydrophilically soluble. In addition, some Berea samples were treated with 1% stearic acid solution. The sample was saturated and aged with 1% stearic acid solution (1% stearic acid dissolved in normal decane) at room temperature for 10 days. The wettability of the rock treated with 1% stearic acid shows a very weak water-wetting for a water/oil system⁽¹⁰⁾.

In a previous work⁽¹²⁾, we reported two processes to alter rock wettability from strongly liquid-wetting to intermediate gas-wetting: process-1 and process-2. In this work, the core samples were treated using process-2. For this process, the core sample with about 10-15% initial water saturation was first saturated with chemical solution using an evacuating system. Then, it was submerged in the same chemical solution; the container was sealed and aged at $T=90^{\circ}\text{C}$ for 3 days. After aging, the core sample was cooled to room temperature and was displaced with dry air to remove all liquids. The core sample, either dry or with some initial water saturation (re-established), was then used for imbibition or flooding tests. In process-2, unlike process-1, we do not heat the dry core at high temperature for stabilizing the chemical adsorption (that is, process-1).

Imbibition and Coreflooding Process

The air-saturated core was hung under an electronic balance and placed in either oil or water to carry out spontaneous imbibition tests (see Figure 2a). For the tests conducted at room temperature, the core was hung on the balance all the time and change in the weight of the core sample vs. time was recorded; for the test conducted at elevated temperature, the core sample and the container were placed in an oven at the test temperature. The weight of the core sample was measured using the electronic balance vs. time.

Coreflooding tests were carried out in the temperature range of about 25°C to 90°C . Figure 2b shows a schematic of the apparatus for coreflooding tests. The core sample was covered with FTP heat-shrinking tubing and placed in a visual coreholder. It was positioned horizontally to avoid gravity effect. A confining pressure of 300 psig was used. In some tests, gas was injected at constant inlet pressure; in others, oil (or water) was injected at constant rate. The produced gas and oil (or water) were separated in the separator installed at the outlet;

the gas and oil (or water) production rates were measured vs. time. The pressure-drop across the core was measured using a Validyne differential pressure transducer. For the tests performed at 90°C, the injected liquids were heated in the pre-heater which was made of a 20-ft coiled copper tubing with an inside diameter of 1 mm, before entering the core.

Results

Wettability Alteration to Intermediate Gas-Wetting

In this section, we will present some aspects of wettability alteration from strong liquid-wetting to intermediate gas-wetting using the chemical treatment process that was described above. Gas recovery and oil imbibition rate by spontaneous oil imbibition are used to characterize the wettability state of the core before and after chemical treatment.

Uniformity of Altered Wettability

Figure 3a shows the core samples (B20-B23) used to examine the uniformity of the altered wettability by chemical treatment. Four cylinder cores were treated with 10% FC-759 at $T=93^{\circ}\text{C}$. After chemical treatment, three of them were cut to make different shapes and fresh surfaces for oil imbibition. Core B23 was not cut; core B21 was cut from the middle along radius; core B22 was cut from the middle along axial; and core B21 was cut from the two ends (see Figure 3a). These four cores were then used for spontaneous oil imbibition testing at room temperature. Figure 4 presents the relevant experimental data for these four cores. T_a represents the aging temperature and T_t represents the test temperature. In order to assess the change in wettability, imbibition data for the untreated Berea sample (B1) is also presented as a reference. The results shown in Fig. 3b reveal that both oil imbibition rate and final gas recovery are similar for the four treated cores. Increase in imbibition surface areas for cores B20-B22 did not raise oil imbibition rate, indicating that the altered wettability by chemical treatment is uniform throughout the cores.

Effect of Initial Wettability State

Berea samples with three wettability states, strongly water-wet, weakly water-wet, and weakly oil-wet were treated with 8% FC-759 to examine the effect of initial wettability state on wettability alteration to intermediate gas-wetting by FC-759 treatment. Untreated Berea sample (B2) was used as a reference for strongly water-wet sample. The measured Amott Index to water (I_w) for core B2 was 1.0. In order to alter the wettability to a weakly water-wet core, Berea sample (B3) was pre-treated with 1% stearic acid solution using the procedure described by Tang and Firoozabadi⁽¹⁰⁾. The measured Amott Index⁽¹⁴⁾ to water (I_w) was 0.18 for core B3 after it was pre-treated with stearic acid solution. For the weakly oil-wet core sample, Berea sample (B4), it was pre-treated with the crude oil from Kagel field, Rio Blanco, Co. The dry core sample was saturated with crude oil and aged at $T=90^{\circ}\text{C}$ for 10 days. Thereafter, the core sample was flooded with hot normal decane until the effluent was colorless. Then, the core was heated for 8 hours at $T=105^{\circ}\text{C}$ to stabilize the adsorption of polar oil components. The measured Amott Index to water (I_w) was zero and to oil (I_o) was about 0.1 for core B4 after it was treated with the crude oil. The core samples with different initial wettability states (strongly water-wet, weakly water-wet and weakly oil-wet) were then treated with 8% FC-759 using the procedure described above. After the cores were treated with 8% FC-759, they were used for spontaneous oil imbibition tests with zero initial water saturation at room temperature.

Figure 4 presents the measured imbibition data for the three Berea samples (B2, B3, and B4). The final gas recovery by spontaneous oil imbibition was about 8% for treated core B2 (initially water-wet), 10% for treated core B3 (initially weakly water-wet), and 15% for treated core B4 (initially weakly oil-wet). The wettability alteration to intermediate gas-wetting using 8% FC-759 treatment was mildly influenced by the initial wettability state of the cores. The trend of the data in Figure 4 suggests that adsorption of FC-759 is not much affected by other polar oil components adsorbed onto the rock surfaces. Clean rock provides the surfaces for FC-759 treatment for the most pronounced wettability alteration. However, the presence of other polar species is not detrimental to wettability alteration to intermediate gas-wetting by FC-759 treatment.

Effect of Initial Liquid Saturation

Figure 5a shows the gas recovery by spontaneous oil imbibition for the core treated at various initial water saturations. The final gas recovery decreased with increase in initial water saturation, indicating a positive effect of initial water saturation on chemical treatment with FC-759. For all the three cores, the final gas recovery was less than 10% (OGIP). A substantial decrease in imbibition rate and final gas recovery was observed due to wettability alteration from strongly liquid-wetting to intermediate gas-wetting. These results are in agreement with our previous study for the treated cores at zero initial water saturation ⁽¹²⁾ and provide strong evidence that wettability alteration to intermediate gas-wetting can be achieved for the cores with about 10-20% initial water saturation.

In the wellbore of gas condensate reservoirs, liquid-condensate dropout could be as high as 60%⁽¹⁵⁾. Therefore, investigation of the effect of initial oil saturation on wettability alteration by FC-759 is of interest. Berea sample (B17) initially saturated with about 10% oil was treated with 10% FC-759 using a treatment procedure similar to the other tests. Thereafter, the core was dried and used for oil imbibition test. Figure 5b shows that gas recovery increased quickly to about 5% (OGIP) at the beginning of the test. After that, the oil imbibed into the core gradually. The oil imbibition continued to the end of the test. The gas recovery by spontaneous oil imbibition at the end of the test was about 33% (OGIP). Higher gas recovery would be expected should we have continued the test. Thus, one may imply that initial oil saturation could reduce the effectiveness of wettability alteration.

In gas condensate reservoirs there is generally some initial water saturation prior to liquid dropout. For practical purposes, further study of the wettability alteration with coexistence of both water and oil saturation is useful. Three cores (B16, B18, and B19) were used for this purpose. We fixed the initial water saturation at 10% and changed the initial oil saturation from zero to 40%. Then the chemical was injected into the cores and the cores were aged at 93°C for three days. After the cores were dried, they were used for imbibition tests. Figure 5c shows the imbibition data for these three cores (B16, B18, and B19). The results reveal that the oil imbibition rate and final gas recovery increases with increase in initial oil saturation at a constant initial water saturation of 10%. Comparison of Figs. 5b and 5c reveals that initial water saturation improves the wettability alteration by FC-759.

Effect of Temperature

In order to study the effect of temperature, we performed spontaneous imbibition tests conducted at various temperatures from 25°C to 93°C. The treated-core sample was placed in a container with a sealed cap and filled with oil. The container was kept in an oven at test

temperature continuously, except for quick measurement of core weight. An untreated core (B5) was tested to establish a reference for studying the effect of temperature on imbibition behavior. For core B5, increase in temperature from 25 to 90°C only showed a small increase in imbibition rate (Figure 6a). Figure 6b shows the data for B15, a Berea core treated with 1% stearic acid solution. The results show that the oil imbibition rate and the final gas recovery were high both at $T=25$ and 90°C. The results also show that stearic acid can establish a weakly water-wetting on Berea sandstone for a water/oil system, but can not establish an intermediate gas-wetting on Berea sandstone for a gas/oil system. Figure 6c shows the experimental data obtained for core B6 when treated with 2% FC-722 twice, at $T=25$, 55, 75, and 88°C, respectively. Oil imbibition rate and the final gas recovery increased systematically with increase in temperature. The imbibition rate at $T=88^\circ\text{C}$ was very high; the final gas recovery was 52% (OGIP), showing a liquid-wet behavior. In order to examine desorption of the chemical from the rock surfaces due to increase in temperature, we dried and weighed core B6 after the tests. The measured data showed that no desorption occurred because the weight of the core remained unchanged. Thereafter, we performed a spontaneous oil imbibition test with core B6 at $T=25^\circ\text{C}$ (defined as run-2 in Figure 6c). The core sample behaved as intermediate gas-wetting again. The final gas recovery for run-2 was only 11% (OGIP), which was nearly the same as that for run-1. This behavior implies that increase in temperature may increase surface energy which improves oil imbibition. Figure 6d shows the data for core Berea B7 treated with 10% FC-759 twice, at $T=25$, 55, 70, and 93°C. The results show that oil imbibition rate and final gas recovery were less influenced with temperature in the 25 to 93°C range. In fact, from $T=25$ to 70°C, the oil imbibition performance did not change appreciably. Even at 93°C, the oil imbibition rate was slow and the final gas recovery was about 27% (OGIP). FC-759 is more effective than FC-722 at high temperatures, indicating that chemical structure is a dominant factor for wettability stability.

Effect of Oil

We compared the oil imbibition behavior in the treated Berea at $T=93^\circ\text{C}$ using both normal tetradecane ($n\text{-C}_{14}$) and normal decane ($n\text{-C}_{10}$). Figure 7 shows the data for the treated and untreated cores. For the untreated core, the oil imbibition rate was slower for $n\text{-C}_{14}$; the final gas recovery was the same for $n\text{-C}_{10}$ and $n\text{-C}_{14}$. For the treated core, both oil imbibition rate and final gas recovery were lower for $n\text{-C}_{14}$. This result implies that the treated core will behave differently with different oils. We have embarked on a set of experiments using condensate liquids in our tests to study the effect of condensates on fluid flow in treated cores.

Wettability Features of the Treated Cores by FC-759 for Water/Oil System

For the cores (B8 and C2) treated with 8% FC-759, we also studied wettability features for the water/oil system. Figure 8a presents the experimental data for water recovery by spontaneous oil imbibition in a 100% water saturated cores, B8 and C2. Figure 8a shows that oil can not imbibe into the water-saturated cores, revealing that the cores B8 and C2 are not preferentially oil-wet. Next, we dried the core samples and saturated them with oil. The oil-saturated cores were then placed in water to perform spontaneous water imbibition testing. Figure 8b presents the oil recovery by spontaneous water imbibition in the oil-saturated cores B8 and C2. About 7% oil was recovered by spontaneous water imbibition from these two cores, indicating that the cores B8 and C2 were not preferentially water-wet either.

The above results reveal that when the core samples (Berea and chalk) were treated with FC-759, it behaved neutrally wet for a water-oil system: neither oil nor water preferentially wets the rock surfaces. The established neutral wetting on Berea sandstone and chalk is stable based on measurements from tests of long duration (we do not present the results here for the sake of brevity).

Implications of Wettability Alteration to Intermediate Gas-Wetting

In a recent work⁽¹²⁾, we showed that flow for a gas/liquid system could be improved significantly through wettability alteration from strong liquid-wetting to intermediate gas-wetting at room temperature. In this work, we study further the effect of wettability alteration to intermediate gas-wetting on (1) recovery efficiency for both gas/oil and water/oil systems, (2) gas and oil relative permeabilities, and (3) injectivity of water or oil. The recovery efficiency tests were performed at room temperature only, whereas relative permeability measurements are conducted both at room temperature and at high temperature.

Two Berea samples, B10 and B11, with a length of 18 cm and a diameter of 2.54 cm were repeatedly used in the following tests. B12 was treated with 8% FC-759 twice and B11 was not treated. All the tests were performed with the coreholder positioned horizontally. The cores were 100% saturated with one phase and the second phase was injected to displace the resident phase.

Recovery for Gas/Oil System

The data of gas recovery by oil injection in the untreated (B11) and treated (B10) cores saturated with air are presented in Figure 9a. Oil was injected at a constant rate of 3 cm³/min. The data show that for the treated core with FC-759, the gas recovery at oil breakthrough increased from 60 to 80% (OGIP); the final gas recovery increased from 80 to 90% (OGIP). The corresponding pressure-drop data for the tests with cores B11 and B10 are presented in Figure 9b. The maximum pressure drop was about 17.5 psi for the untreated core (B11) and about 7.2 psi for the treated core (B10). After oil breakthrough, the pressure-drop gradually decreased and stabilized at 7.6 psi for the untreated core (B11) and at 5.6 psi for the treated core (B10). Decrease in pressure-drop after wettability alteration indicates an increase in oil injectivity in porous media.

Recovery for Oil/Water System

Figure 10a shows the results for water injection in 100% oil-saturated cores. The water injection rate was 4 cm³/min. For the treated core (B10), the oil recovery at water breakthrough was about 56% (OOIP) and the final recovery was about 72% (OOIP). For the treated core (B10), about 16% (OOIP) oil was produced after water breakthrough, indicating the invading phase (water) was not preferentially wetting the rock surface. For the untreated core (B11), the oil recovery at water breakthrough was about 53% (OOIP) and the final recovery was about 54% (OOIP). The oil recovery after water breakthrough was negligible, indicating a typical process of wetting phase (water) displacing a non-wetting phase (oil). This result is consistent with the results obtained by Tweheyo et al⁽¹⁶⁾. The pressure-drop data presented in Figure 10b also indicate a decrease after wettability alteration. The maximum pressure-drop for the untreated core (B11) was 6.5 psi and it then stabilized at 5.6 psi after water breakthrough. For the treated core (B10), the maximum pressure-drop was 2.9 psi and it then stabilized at 1.4 psi after water breakthrough. The pressure drop decreased about 3.5 times after wettability

alteration, indicating a significant increase of water injectivity in the oil saturated core. This result is in line with the work reported by Penny et al (1983)⁽⁸⁾.

Figure 11a shows the experimental data for oil injection in water-saturated cores. The oil injection rate was 4 cm³/min. For the untreated core (B11), water recovery at oil breakthrough was about 30%, and the final recovery was about 50% (WOIP). Nearly two-fifths of the recovered water was produced after oil breakthrough, indicating a non-wetting phase (oil) displacing a wetting phase (water). For the treated core (B10), the water recovery at oil breakthrough was about 51% (WOIP) and the final recovery was about 62 % (WOIP). This behavior also indicates that the oil phase (the invading phase) was not preferentially wetting the rock. The corresponding pressure-drop data for oil displacing water are presented in Figure 11b. The maximum pressure-drop for the untreated core was about 3.4 psi; it then stabilized at 2 psi. For the treated core, the maximum pressure-drop was about 1.7 psi and it then stabilized at 0.8 psi. The oil injectivity in the water-saturated core increased 2 times with the alteration of wettability.

The results above show that after wettability alteration from strong liquid-wetting to intermediate gas-wetting, gas recovery by oil injection, oil recovery by water injection, and water recovery by oil injection were improved significantly. In addition, oil injectivity in the gas-saturated core, oil injectivity in water-saturated core, and the water injectivity in the oil-saturated core were improved significantly. All these results imply that wettability alteration through FC-759 treatment can also be applied to oil reservoirs and aquifers for the purpose of improving water and oil injectivity and productivity in water-oil flow.

Reduction of Oil Saturation in Porous Media by Dry Gas Injection

In some gas condensate reservoirs, liquid dropout accumulation near the wellbore can cause sharp decline in gas production^(16,17). Removal of liquids from the wellbore has been a challenge. In this work, we study the effect of wettability alteration on oil removal from a core by injecting dry gas. Two Berea samples, B13 (treated with 10% FC-759 twice) and B14 (untreated) were saturated with oil (n-C₁₀). Then they were subjected to dry air injection at a constant pressure gradient of 0.056 psi/cm. The oil saturation was measured by weighing the core; thus the measured oil saturation is an average value. The tests were carried out at $T=25$ and 90°C .

Figure 12a presents the average oil saturation (n-C₁₀) vs. time for the treated and untreated cores at $T=25^{\circ}\text{C}$. Oil saturation in both cores decreased quickly from 100 to about 60% during the first 20 minutes. Then, oil saturation decreased slower. The oil saturation in the treated core (B13) remained lower than that in the untreated core (B14), showing higher oil mobility in the treated core. At injection time $t=200$ minutes, the oil saturation in the treated core (B13) was about 30% and in the untreated core (B14) was about 41%. The final oil saturation in the treated core (B13) was 23%; in the untreated core (B14), it was 35%.

Results at $T=90^{\circ}\text{C}$ are presented in Figure 12b. At $t<200$ minutes, the oil saturation decreased with a trend similar to the test at $T=25^{\circ}\text{C}$. Thereafter, the oil saturation in both cores continued decreasing at a lower rate. The oil saturation in the treated core (B13) was about 20% lower than that in the untreated core (B14). At $t=2400$ minutes, the oil saturation in the treated core (B13) reached zero and the oil saturation in the untreated core (B14) reached 17%. Comparing the results shown in Figures 12a and 12b, one may assume that at high temperatures, oil saturation could be further decreased. We assume that in addition to the wettability alteration, the phase-behavior effect also reduces oil saturation in porous media at high temperatures.

Gas and Oil Relative Permeabilities

Figure 13a shows the measured gas and oil relative permeabilities for the untreated core (B14) and treated core (B15) at 90°C. Initial water saturation was zero and the oil phase was normal decane (n-C₁₀). The results show that the wettability alteration from strong liquid-wetting to intermediate gas-wetting resulted in (1) the oil saturation at the point for $k_{ro} = k_{rg}$ reduced from 0.55 to 0.48 PV; (2) the cross point relative permeability increased from 0.04 to 0.1 PV; (3) gas relative permeability decreased, but oil relative permeability increased significantly; and (4) the residual oil saturation decreased from 0.48 to 0.1 PV. These results are in line with those obtained at room temperature (Tang and Firoozabadi, 2000). Figure 13b shows the measured gas and oil relative permeabilities for the treated core (B15) at 90°C. Both n-C₁₀ and n-C₁₄ were used. The results show that the gas relative permeability decreased and oil relative permeability increased when the oil phase was changed from n-C₁₀ to n-C₁₄. This trend is in agreement with our imbibition study shown in Figure 7. As was stated earlier, we are currently working with condensate liquids and the results will be the subject of a forthcoming publication.

Discussions and Conclusions

In this work, we have demonstrated that the wettability of Berea and chalk can be altered to intermediate gas-wetting using FC-759 for a temperature range of 25-93°C with initial water and oil saturations. From wettability alteration to intermediate gas-wetting, we showed: (1) improved recovery performance for both gas/oil and oil/water systems; (2) increased oil phase mobility and decrease in residual oil saturation for a gas/oil system; (3) reduced oil saturation in porous media through injecting dry gas at both room and elevated temperatures; and (4) increased oil or water injectivity in water/oil flow.

In addition, in the course of the experiments, we did not observe core damage due to treatment with FC-759. Visual examinations show that fine particles of the Berea and chalk become more stable after treatment with FC-759. Therefore, sand production could also reduce by adsorption of FC-759 onto the rock surfaces.

We are currently searching for new chemicals that are very effective for wettability alteration to intermediate gas-wetting. Also, we are currently focusing on tests at reservoir conditions including using reservoir gas condensate fluids. The results will be published in due time.

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Table 1 **Core Properties and Other Relevant Data**

Core	k _a (md)	f (%)	L (cm)	d (cm)	T _r (°C)	Chemical treatment	Fluid systems
B1	316	20.1	5.8	2.5	25/93	-	g/o
B2	308	20.0	5.7	2.5	25	-	g/o
B3 ^a	310	20.3	6.2	2.5	25	8% FC-759	g/o
B4 ^b	301	20.5	5.9	2.5	25	8% FC-759	g/o
B5	321	20.3	6.1	2.5	25/90	-	g/o
B6	311	20.1	5.7	2.5	25/55/88	2% FC-722	g/o
B7	323	20.5	6.2	2.5	25/50/70/93	10% FC-759	g/o
B8	317	20.1	5.9	2.5	25	8% FC-759	w/o
B9	296	19.9	6.2	2.5	25	10% FC-759	g/o
B10	322	22.4	18.0	2.5	25	8% FC-759	g/o
B11	318	22.2	18.2	2.5	25	-	g/o, w/o
B13	308	22.0	17.8	2.5	25/90	10% FC-759	g/o
B14	321	21.9	18.1	2.5	25/90	-	g/o
B15	310	21.8	18.4	2.5	90	10% FC-759	g/o
B16	293	20.1	6.2	2.5	25	10% FC-759	g/o
B17	289	20.0	5.8	2.5	25	10% FC-759	g/o
B18	303	20.1	6.0	2.5	25	10% FC-759	g/o
B19	327	20.5	5.6	2.5	25	10% FC-759	g/o
B20 ^c	310	20.3	6.2	2.5	25	10% FC-759	g/o
B21 ^c	289	20.0	5.7	2.5	25	10% FC-759	g/o
B22 ^c	312	20.4	6.1	2.5	25	10% FC-759	g/o
B23	309	20.3	6.2	2.5	25	10% FC-759	g/o
B24	279	19.9	6.0	2.5	25	10% FC-759	g/o
B25 ^d	311	20.1	6.3	2.5	93	10% FC-759	g/o
B26	301	20.0	6.0	2.5	93	10% FC-759	g/o
C-2	1.31	31.2	6.7	2.2	25	8% FC-759	g/o, w/o

Note: ^a pretreated with stearic acid; ^b pretreated with crude oil; ^c cut cores; ^d n-C₁₄ was oil phase

R_f-Flourochemical

A -Anionic group

N -Nonionic group

W≠X≠Y≠Z

Fig.1 Chemical Structure of FC-759 (Linert, 1997)

Fig.2a Schematic of the Apparatus for Spontaneous Imbibition Tests

Fig.2b Schematic of the Apparatus for Coreflooding Tests

B-23

B-20

B-21

B-22

Figure 3a Schematic of the Cores after Cutting

Fig. 3b Gas Recovery by Spontaneous Oil Imbibition for Cores Treated with 10% FC-759 before and after Cut

Fig.4 Effect of Initial Wettability on Wettability Alteration by 8% FC-759

Fig.5a Effect of Initial Water Saturation on Wettability Alteration by 8% FC-759

Fig.5b Effect of Initial Oil Saturation on Wettability Alteration by 10% FC-759

Fig.5c Effect of Initial Water and Oil Saturation on Wettability Alteration by 10% FC-759

Fig.6a Effect of Temperature on Spontaneous Oil Imbibition for Untreated Berea

Fig. 6b Effect of Temperature on Spontaneous Oil Imbibition Treated Berea with 1% Stearic Acid

Fig.6c Effect of Temperature on Spontaneous Oil Imbibition for Berea Samples Treated with 2% FC-722.

Fig.6d Effect of Temperature on Spontaneous Oil Imbibition for Berea Sample Treated With 10% FC-759

Fig.7 Spontaneous Imbibition of nC₁₀ and nC₁₄ for Berea Sample Treated With 10% FC-759

Fig.8a Water Recovery by Spontaneous Oil Imbibition for the Cores Treated with 8% FC-759

Fig.8b Oil Recovery by Spontaneous Water Imbibition for the Cores Treated with 8% FC-759

Fig.9a Effect of Wettability Alteration on Gas Recovery by Oil Injection.

Fig. 9b. Effect of Wettability Alteration on Pressure Drop for Oil Injection in Gas Saturated Berea

Fig.10a Effect of Wettability Alteration Oil Recovery by Water Injection

Fig.10b Effect of Wettability Alteration on Pressure Drop for Water Injection in Oil Saturated Cores

Fig.11a Effect of Wettability Alteration on Water Recovery by Oil Injection

Fig.11b Effect of Wettability Alteration on Pressure Drop for Oil Injection in Water Saturated Cores

Fig.12a Effect of Wettability on Reduction of Oil Saturation by Dry Gas Injection at Room Temperature

Fig.12b Effect of Wettability on Reduction of Oil Saturation by Dry Gas Injection at High Temperature

Fig.13a Gas and Oil Relative Permeabilities for Treated and Untreated Cores at $T=90^\circ\text{C}$: nC-10

Fig.13b Gas and Oil Relative Permeabilities for Treated Berea at $T=90^{\circ}\text{C}$ for nC-10 and nC-14

Chapter 3 - Work of Formation for Spherical and Cap-Shaped Clusters: Single Component Systems

Abbas Firoozabadi

The work of cluster formation, W , is a major parameter in the nucleation rate expression $J_s = a \exp[-W^*/kT]$ where W^* is the work of the cluster at the critical size, and J_s is the stationary rate of nucleation, a is the kinetic factor, T is the absolute temperature, and k is the Boltzmann constant. The work of cluster formation is also directly useful in the understanding of a large number of phenomena including the delay period, the memory effects (lack of reproducibility), and the most probable location for the formation of a new phase. Work of cluster formation is also a key parameter in the understanding of wettability alteration to intermediate gas-wetting.

In the following, we will first derive the work of cluster formation for the spherical shape, then proceed to cap-shaped and lens-shaped clusters.

Spherical Clusters

Consider Fig. 1 which depicts the state of N molecules in the initial state (State I) of uniform density at temperature T and pressure P (Fig. 1a). The final state (State II) corresponds to the homogeneous formation of a spherical cluster of n molecules at temperature T and pressure P in the mother phase.

Let us write the expression for the Gibbs free energy of the total system at state I,

$$G^I = Nm \quad (1)$$

In the above equation, m is the chemical potential per molecule. The Gibbs free energy of state II is given by

$$G^{II} = PV + A^{II} \quad (2)$$

Note that in Eq. 2, $V = V_{N-n} + V_n$; [V_{N-n} and V_n are defined based on the equimolecular dividing surface (EDS).] and A^{II} is the total Helmholtz free energy at state II. We have shown that in Eq. 2, P is the pressure of the mother phase.¹ The Helmholtz free state at state II is given by

$$A^{II} = [(N-n)m - pV_{N-n}] + [nm^I(P_n) - P_n V_n] + f(V_n) \quad (3)$$

In Eq. 3, $f(V_n)$ is the surface energy of the spherical cluster and $m^I(P_n)$ is chemical potential of the cluster per molecule. Combining Eqs. 2 and 3 one obtains,

$$G^{II} = -V_n(P_n - P) + n[m^I(P_n) - m] + Nm + f(V_n) \quad (4)$$

The difference between G'' and G' can be obtained from Eqs. 1 and 4,

$$\Delta G = G'' - G' = -(P_n - P)V_n + n[\mathbf{m}''(P_n) - \mathbf{m}'] + \mathbf{f}(V_n) \quad (5)$$

The work of cluster formation $W = \Delta G$ is, therefore,

$$W = -(P_n - P)V_n + [\mathbf{m}''(P_n) - \mathbf{m}']n + \mathbf{f}(V_n) \quad (6)$$

Note that three terms contribute to the work of cluster formation. The first term is from expansion, the second term is from the non-equilibrium effect, and the third term is from the interfacial effect.

Next we will assume that there is mechanical equilibrium. The condition for mechanical equilibrium is given by $(\partial G_2 / \partial V_n)_{n,p_n} = 0$. Therefore, from Eq. 4,

$$P_n = P + \frac{d\mathbf{f}}{dV_n} \quad (7)$$

For an equimolecular dividing surface (EDS),

$$\mathbf{f}(V_n) = \mathbf{s}_n S_n \quad (8)$$

where $\mathbf{s}_n$ is the interfacial tension and S_n is the surface area of the cluster. For spherical clusters $S_n = (36\mathbf{p})^{1/3} V_n^{2/3}$.

Let us assume that the interfacial tension is independent of the size of the clusters, then $\mathbf{s}_n = \mathbf{s} = \text{constant}$, and

$$\mathbf{f}(V_n) = (36\mathbf{p})^{1/3} \mathbf{s} V_n^{2/3} \quad (9)$$

From Eqs. 7 and 9,

$$P_n = P + [(2/3)(36\mathbf{p})^{1/3}] \frac{\mathbf{s}}{V_n^{1/3}} \quad (10)$$

For a sphere, $V_n = (4/3)\mathbf{p}r^3$ (r is the cluster diameter); an alternative form of Eq. 10 is

$$P_n = P + \frac{2\mathbf{s}}{r} \quad (11)$$

Eq. 11 is the Laplace equation.

In nucleation theory, instead of the true driving force $-\left[\mu^H(P_n) - \mu^L(P)\right]$, the driving force in the form of $-\left[\mu^H(P) - \mu^L(P)\right]$ is used. This choice does not effect W . We can write Eq. 6 in the following form,

$$W = -(P_n - P)V_n + [\mu^H(P_n) - \mu^H(P)]n + [\mu^H(P) - \mu^L(P)]n + f(V_n) \quad (12)$$

Note that in the third term on the right of Eq. 12 although the pressure and temperature of states I and II are the same, the chemical potentials are generally different because the fluid (and solid) states are not the same. The difference between $\mu^H(P)$ and $\mu^L(P)$ in Eq. 12 is shown by $\Delta\mu = [\mu^L(P) - \mu^H(P)]$ and is defined in the nucleation literature as the driving force. With this definition, Eq. 12 can be rewritten as

$$W = -(P_n - P)V_n + [\mu^H(P_n) - \mu^H(P)]n - n\Delta\mu + f(V_n) \quad (13)$$

The second term on the right side of Eq. 13 can be evaluated using $[d\mu = (V_n/n)dP]_T$,

$$\mu^H(P_n) - \mu^H(P) = (1/n) \int_P^{P_n} V_n(P) dP \quad (14)$$

For an incompressible liquid or solid cluster, Eq. 14 becomes

$$\mu^H(P_n) - \mu^H(P) = v_o(P_n - P) \quad (15)$$

where v_o is the molecular volume.

For an ideal gas $PV_n = nkT$. Substitution of $V_n = nkT/P$ in Eq. 14 provides

$$\mu^H(P_n) - \mu^H(P) = kT \ln \frac{P_n}{P} \quad (16)$$

We can now write the expression for the work of cluster formation.

Incompressible Clusters – For an incompressible cluster, the first and second terms on the right side of Eq. 13 cancel out (using Eq. 15) and, therefore,

$$W = -n\Delta\mu + f(V_n) \quad (17)$$

Eq. 17 can be expressed in various forms in terms of the cluster volume, V_n , number of molecules in the cluster, n , and the radius of the cluster, r . In terms of cluster volume, the work of cluster formation is given by

$$W(V_n) = -(V_n/v_o)\Delta\mu + (36\pi)^{1/3} \sigma V_n^{2/3} \quad (18)$$

The work of cluster formation in terms of n and r are

$$W(n) = -n\Delta m + (36p_o^2)^{1/3} S n^{2/3} \quad (19)$$

$$W(r) = -(4p/3v_o)r^3 \Delta m + 4p^2 S, \quad (20)$$

respectively.

Gas Clusters – When a gas cluster follows an ideal gas behavior, the second expression in the right side of Eq. 13 can be simplified using Eq. 16. However, before proceeding to this step, let us simplify Eq. 13 by substituting Eqs. 10 and 9 for its first and fourth terms,

$$W = [\mathbf{m}^H(P_n) - \mathbf{m}^H(P) - \Delta m]n + (1/3)(36m)^{1/3} S V_n^{2/3} \quad (21)$$

The second term on the right side of Eq. 21 is equal to $(1/3)SS$ where S is the surface area. The terms in the bracket are simply $[\mathbf{m}^H(P_n) - \mathbf{m}^H(P)]$ which becomes zero when $\mathbf{m}^H(P_n) = \mathbf{m}^H(P)$; this is the condition of equilibrium, but it is an unstable equilibrium due to the fact that it corresponds to a maximum in ΔG , not a minimum as we see later.

With the substitution of Eq. 16 for $\mathbf{m}^H(P_n) - \mathbf{m}^H(P)$ and $n = P_n V_n / kT$ and P_n from Eq. 10, Eq. 21 transforms into

$$W = -\left\{(\Delta m / kT) - \ln[1 + (2/3)(36p)^{1/3} S / (P V_n^{1/3})]\right\} \\ \times [P + (2/3)(36p)^{1/3} S / V_n^{1/3}] V_n + (1/3)(36p)^{1/3} S V_n^{2/3} \quad (22)$$

Eq. 22 can also be expressed as a function of n and r ,

$$W(n) = -n[\Delta m - kT \ln(P_n / P)] + (1/3)(36p)^{1/3} S (kT / P_n)^{2/3} n^{2/3} \quad (23)$$

and

$$W(r) = -(4p/3)(\Delta m / kT) - \ln[1 + 2S / Pr](P + 2S / r)r^3 + \frac{4}{3} p^2 S, \quad (24)$$

respectively.

Cap-Shaped Clusters

Consider Fig. 2; in state I, there is no cluster formation, in state II, a cap-shaped cluster is formed on the substrate. We are interested to derive the expression for the work of cluster formation.

The Gibbs free energy of the system at state I is given by,

$$G^I = N\mathbf{m}^I + \mathbf{f}_{so} + G_s \quad (25)$$

where $\mathbf{f}_{so}$ is the surface energy of the substrate-mother phase interface and G_s is the Gibbs free energy of the bulk-phase substrate. $\mathbf{f}_{so} = \mathbf{s}_s A_s$ where $\mathbf{s}$ is the specific surface energy of the mother-phase-substrate interface, and A_s is the surface area of the substrate.

The Gibbs free energy of the system at state II is given by,

$$G^{II} = A^{II} + PV \quad (26)$$

where the Helmholtz free energy is obtained from,

$$A^{II} = [(N-n)\mathbf{m}^I - PV_{N-n}] + [n\mathbf{m}(P_n) - P_n V_n] + \mathbf{f} + \mathbf{f}_s + G_s \quad (27)$$

In Eq. 27, $\mathbf{f}$ is the surface energy of the interface between 1) the mother phase and the cluster, and 2) the cluster and the substrate. In the same equation, $\mathbf{f}_s$ is the surface free energy of the interface between the mother phase and the substrate minus the portion of the base of the cluster. Substituting Eq. 27 into Eq. 26 and using $PV = P(V_{N-n} + V_n)$,

$$G^{II} = [n\mathbf{m}^I(P_n) - n\mathbf{m}^I(P)] - [P_n - P]V_n + N\mathbf{m}^I + \mathbf{f} + \mathbf{f}_s + G_s \quad (28)$$

The work of cluster formation is obtained by subtracting Eq. 28 from 25,

$$W = G^{II} - G^I = \Delta G = [n\mathbf{m}^I(P_n) - n\mathbf{m}^I(P)] - [P_n - P]V_n + (\mathbf{f} + \mathbf{f}_s - \mathbf{f}_{so}) \quad (29)$$

An alternative form of Eq. 29 is obtained by defining $\Delta\mathbf{m} = \mathbf{m}^I(P) - \mathbf{m}^I(P_n)$,

$$W = [n\mathbf{m}^I(P_n) - n\mathbf{m}^I(P)] - n\Delta\mathbf{m} - [P_n - P]V_n + (\mathbf{f} + \mathbf{f}_s - \mathbf{f}_{so}) \quad (30)$$

The condition for mechanical equilibrium of the system II is given by $\partial G^{II} / \partial V_n = 0$ where the number of molecules in the cluster is held constant. As a result, from Eq. 29 one obtains,

$$P_n = P + \frac{d(\mathbf{f} + \mathbf{f}_s)}{dV_n} = 0 \quad (31)$$

In order to proceed further, we will obtain explicit expressions for surface free energies $\mathbf{f}$ and $\mathbf{f}_s$ and use the Young equation.

Derivation of the Young Equation – Young's equation is the condition for equilibrium shape of a spherical liquid drop on a substrate. Such a shape is often called a cap. Let us

consider a cap-shaped cluster sketched in Fig. 3. The specific surface energies are also shown in the same figure. The surface area of the cap dome is given by $2\mathbf{p}^2(1 - \cos \mathbf{q})$. The surface area of the cluster is given by $\mathbf{p}^2 \sin^2 \mathbf{q}$.

The surface energy of the cluster (base and dome) is given by

$$\mathbf{f}(r) = 2\mathbf{p}^2(1 - \cos \mathbf{q})\mathbf{s} + (\mathbf{p}^2 \sin^2 \mathbf{q})\mathbf{s}_i. \quad (32)$$

The surface energy of the substrate (minus the portion from the base of the cluster) is given by,

$$\mathbf{f}_s(T) = [A_s - \mathbf{p}^2 \sin^2 \mathbf{q}]\mathbf{s}_s \quad (33)$$

where A_s is the total surface area of the substrate. The total surface free energy of the system in Fig. 3 is, therefore, given by

$$\mathbf{f}_t = \mathbf{f} + \mathbf{f}_s = 2\mathbf{p}^2 \left[(1 - \cos \mathbf{q})\mathbf{s} + \frac{1}{2}(1 - \cos^2 \mathbf{q})(\mathbf{s}_i - \mathbf{s}_s) \right] + \mathbf{s}_s A_s \quad (34)$$

The volume of the cluster is given by,

$$V = [\mathbf{y}(\mathbf{q})](4/3)\mathbf{p}^3 \quad (35)$$

where $\mathbf{y}(\mathbf{q})$ is the shape factor,

$$\mathbf{y}(\mathbf{q}) = (1/4)(2 + \cos \mathbf{q})(1 - \cos \mathbf{q})^2 = (1/4)(2 - 3 \cos \mathbf{q} + \cos^3 \mathbf{q}) \quad (36)$$

In a cluster of n molecules, for a given volume of V , the shape of the cluster is determined by a minimum of $\mathbf{f}_t$ with respect to variations of r and $\cos \mathbf{q}$, then

$$\mathbf{f}_t = 2\mathbf{p}^2 \left[(1 - x)\mathbf{s} + \frac{1}{2}(1 - x^2)(\mathbf{s}_i - \mathbf{s}_s) \right] + \mathbf{s}_s A_s \quad (37)$$

From $d\mathbf{f}_t = 0$

$$2 \left[(1 - x)\mathbf{s} + \frac{1}{2}(1 - x^2)(\mathbf{s}_i - \mathbf{s}_s) \right] \frac{dr}{r} - [\mathbf{s} + x(\mathbf{s}_i - \mathbf{s}_s)] dx = 0 \quad (38)$$

The volume of the cluster is given by,

$$V = \frac{1}{3}\mathbf{p}^3(2 - 3x + x^3) \quad (39)$$

From $dV = 0$

$$(2 - 3x + x^3) \frac{dr}{r} + (1 - x^2) dx = 0 \quad (40)$$

Combining Eqs 38 and 40 , one obtains the Young equation,

$$\boxed{\mathbf{s} \cos \mathbf{q} = \mathbf{s}_s - \mathbf{s}_i} \quad (41)$$

The above equation is also valid for a crystal cap in addition to a liquid cap. A similar approach can be use to derive the Young's equation for a cluster on a conical substrate.

Combining Eqs. 30, 34, 36, and 41 one obtains,

$$W = [\mathbf{m}^I(P_n) - \mathbf{m}^I(P)]n - n\Delta\mathbf{m} - [P_n - P]V_n + 4\mathbf{y}(\mathbf{q})\mathbf{p}r^2\mathbf{s} \quad (42)$$

Note that Eq. 42 is similar to Eq. 13. The expressions for the work cluster formation for liquid and gas cap-shaped clusters can be obtained in a similar manner as those for the spherical clusters.

Driving Force ($\Delta\mathbf{m}$)

We have defined the thermodynamic driving force for the first-order phase transition as,

$$\Delta\mathbf{m}(T, P) = \mathbf{m}^I(T, P) - \mathbf{m}^I(T, P_e) \quad (35)$$

In the following, basic expressions for $\Delta\mathbf{m}$ are derived.

Condensation from Vapor at Constant T – Condensation from vapor at temperature T occurs when $P > P_e$ where P_e is the equilibrium pressure at T . From $d\mathbf{m} = vdp$, (state I is vapor)

$$\mathbf{m}^I(T, P) - \mathbf{m}^I(T, P_e) = \int_{P_e}^P v dp \quad (36)$$

For an ideal gas $v = kT / P$,

$$\mathbf{m}^I(T, P) - \mathbf{m}^I(T, P_e) = \int_{P_e}^P \frac{kT}{p} dp = kT \ln \frac{P}{P_e} \quad (37)$$

Therefore,

$$\mathbf{m}^I(T, P) = \mathbf{m}^I(T, P_e) + kT \ln \frac{P}{P_e} \quad (38)$$

Next we require the expression for $\mathbf{m}^H(T, P) - \mathbf{m}^H(T, P_e)$, which is already available from Eq. 15 with the assumption of liquid incompressibility. It is rewritten in the following

$$\mathbf{m}^H(T, P) = \mathbf{m}^H(T, P_e) + v_o(P_e - P) \quad (39)$$

At equilibrium (T and P_e),

$$\mathbf{m}^l(T, P_e) = \mathbf{m}^H(T, P_e) \quad (40)$$

Therefore, combining Eqs. 35 and 38-40

$$\Delta \mathbf{m}(T, P) = kT \ln \frac{P}{P_e} + v_o(P_e - P) \quad (41)$$

Evaporation from Liquid at Constant T

Evaporation from a liquid can occur at constant T when $P < P_e$. The expression for chemical potential of state I (that is, liquid state) is

$$\mathbf{m}^l(T, P) = \mathbf{m}^l(T, P_e) + v_o(P - P_e) \quad (42)$$

where it is assumed that the liquid is incompressible. The chemical potential in the vapor (state II) is given by

$$\mathbf{m}^H(T, P) = \mathbf{m}^H(T, P_e) + kT \ln \frac{P_e}{P} \quad (43)$$

Combining Eqs. 35, 42, and 43

$$\Delta \mathbf{m} = v_o(P - P_e) + kT \ln \frac{P_e}{P} \quad (44)$$

Reference

Firoozabadi, A.: Thermodynamics of Hydrocarbon Reservoirs, McGraw-Hill, 1999, Chapter II.

Fig. 1 – The states before and after formation of one n -molecule spherical cluster at constant T and P . Note the pressure in the cluster (P_n) is generally different from P .

Fig. 2 – The states before and after formation of an n -molecule cap-shaped cluster at constant T and P .

Fig. 3 – Cap-shaped liquid cluster on a flat substrate.