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THERMODYNAMICS OF COMPLEX FLUIDS FOR CHEMICAL ENHANCED OIL RECOVERY

A Dissertation in

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by

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ABSTRACT

Chemical enhanced oil recovery methods have significant potential to improve oil recovery after waterflooding. It is relatively easy to improve recovery in the lab under controlled conditions. However, field-scale implementations do not yield the same recovery results for a variety of reasons that include different mixing levels from the lab to the field, and also that species travel at different velocities. Moreover, the modeling of physicochemical phenomena, which are involved in the process, can be inaccurate or lack predictive capabilities. Such phenomena include phase behavior, viscosity, and reaction kinetics modeling. In this dissertation, we present modeling improvements and a better understanding of those physicochemical processes. The improvements will help to model accurately and to design successfully improved oil recovery scenarios.

This dissertation presents the following research outcomes to model physicochemical phenomena involved in chemical enhanced oil recovery. Chapter 1 covers introductory remarks on chemical enhanced oil recovery. Chapter 2 focusses on the experimental study of alkali-cosolvent phase behavior using acidic crude oil. We study the possibility of using alkali for in situ surfactant generation, over costly synthetic surfactants. The chapter proposes a mechanism that explains the formation of water-in-oil macroemulsion, which is traditionally overlooked. Chapter 3 discusses an updated flash calculation algorithm with variable characteristic length in microemulsion phase. Chapter 6 presents a microemulsion phase behavior equation of state algorithm that accounts for equilibrium K-values, and surfactant partitioning. For the first time, we propose equations to constrain the size of two-phase lobes. These constraints are based on constant K-value limiting conditions. Chapter 5 presents a compositional viscosity model for microemulsion systems. We present a 'viscosity map' approach that accounts for the percolation threshold locus in compositional space. The compositional aspect of microemulsion viscosity is typically overlooked in the literature. Chapter 6 is focused on modeling the effects of reaction kinetics and dispersion during low salinity waterflooding. Reaction kinetics is typically ignored in reservoir simulation. We show that oil recovery is affected when reaction kinetics is included in modeling, for example, recovery fronts are delayed based on the ratio of convection and reaction rates. Chapter 7 concludes this dissertation. The common theme of this dissertation addresses the thermodynamics of complex fluids in the context of chemical enhanced oil recovery.

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Dedication

Bismillah. I dedicate this dissertation to my mother Klara Magzymova and my father Balgabay Magzymov for their unconditional love, endless support, and genuine wisdom.

Chapter 1 Introductory remarks

This section describes the problem statement and brief review of motivations, objectives, and the structure of this dissertation.

Problem statement

A significant amount of oil is left behind in reservoirs after water flooding. The ultimate oil recovery is limited by displacement and sweep efficiencies (Lake et al., 2014). Displacement efficiency is defined as the ratio of displaced oil to contacted oil volume. Sweep efficiency is defined as the ratio of the volume of contacted oil to the volume of oil in place. Both efficiencies are improved by chemical enhanced oil recovery techniques.

Oil is trapped in porous media due to capillary forces. Viscous forces must overcome the capillary forces to mobilize the oil. Under multiphase flow conditions, the ultimate amount of recoverable oil is limited by displacement efficiency, such as trapped residual oil saturation (Humphry et al., 2014).

Residual oil saturation is oil trapped in a porous media by capillary forces. Saturation is defined as a fraction of pore space volume occupied by a certain phase. Residual oil saturation is a function of viscous forces, surface tension forces, gravitational forces, wettability state, and pore geometry (Mohanty and Salter, 1983). The effects of those parameters are shown in Figure 1 below. Chemical enhanced oil recovery techniques are focused on both improving sweep and displacement efficiencies by mobilizing the oil (Lake et al., 2014). This is accomplished by the application of chemicals, such as surfactants, polymers, alkali, and salts, to change viscous forces, surface forces, and the wettability of the rock.



Figure 1 Schematic capillary desaturation curve. Adopted from Lake et al. (2014)

Figure 1 shows how capillary number affects residual oil saturation. The capillary number is defined as a ratio of viscous forces to capillary forces, $Ca = \frac{\mu v}{\gamma}$, where γ is the interfacial tension between oil and brine, μ is the viscosity of injected brine, and v is the brine velocity in the pores. To reduce the residual oil saturation (improve displacement efficiency), we need to manipulate the viscous force, surface force, and wettability of the

rock. Thus, there is a need for accurate predictive models that can explain and capture processes for reducing residual oil saturation.

In this dissertation, we also focus on developing microemulsion phase behavior equation-of-state that helps to estimate phase compositions and to find the optimum conditions more exactly as variables change during chemical flood. Moreover, we develop a compositional viscosity model that improves estimation of viscous forces. Furthermore, we evaluate the effect of reaction kinetics and dispersion during low-salinity waterflooding that affects the wettability state. The hypotheses of this research are as follows:

- 1. Alkali and acidic crude oil can generate *enough* insitu surfactants for enhanced oil recovery applications for high acidic crude oil.
- 2. Three-phase characteristic length should vary as a function of formulation variables, instead of being constant in HLD-NAC based models.
- 3. Tie triangle K-values can be used to restrict the size of two-phase lobes.
- 4. Thee pseudocomponent compositional dependence of microemulsion viscosity can be captured by a suspension model, continuity model, and percolation threshold locus.
- 5. Wettability alteration process for both carbonate and sandstone can be modelled using a unified binary model. Accounting for reaction kinetics and dispersion may vastly impact the oil recovery estimates during low-salinity waterflooding.

Research objectives

In this dissertation, we present physical models that are essential for chemical enhanced oil recovery applications. The objectives of this research are to:

- Investigate the use of alkali to generate insitu surfactant and favorable phase behavior for a high total-acid-number (TAN) crude oil for potential field application. We model the alkali/crude oil system using both experimental and analytical methods.
- 2. Extend physics-based phase behavior models, in terms of accuracy, thermodynamic consistency, and functionality. Interfacial tension strongly depends on phase behavior. Therefore, having a representable phase behavior model is essential for predictions and the design of chemical enhanced oil recovery projects.
- Develop a physics-based model that captures microemulsion viscosity variation in compositional space. We aim to develop an algorithm to generate a 'viscosity map' in compositional space for pseudoternary diagram at fixed temperature and pressure.
- 4. Construct a unified mechanistic model of wettability alteration that can be adapted for both sandstone and carbonate reservoirs based on pseudocomponent identification of the wettability controlling species for both rock types. We also examine the effects of reaction kinetics and dispersion that

are incorporated through dimensionless groups such as the Damköhler and the Peclet number.

Dissertation structure

This dissertation is separated into five chapters that focus on the objectives presented above. Each chapter has its own literature review, methodology, and results sections. Chapter 2 is focused on the experimental and analytical analysis of alkali-salt-alcohol phase behavior with high acid number crude oil. Chapter 3 develops a variable characteristic length model for microemulsion phase flash calculation. Chapter 4 presents an improved phase behavior model for surfactant-oil-water systems using a K-value limiting case approach. Chapter 5 describes the compositional dependent viscosity model for the microemulsion phase. Chapter 6 demonstrates the effects of reaction kinetics and dispersion during low salinity waterflooding. The last Chapter 7 summarizes each Chapter and presents the main conclusions of the research and recommendations for future research. The common theme for this dissertation is to improve modeling of physical phenomena involved in chemical enhanced oil recovery.

Chapter 2 Experimental Analysis of Alkali-Salt-Alcohol Phase Behavior with Crude Oil of High Acid Number

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Chapter Summary

The primary aim of this research is to characterize and model phase behavior of alkali/crude oil systems using crude oil and chemicals provided by OMV company. The significant improved oil recovery post-polymer flooding is evident from coreflood alkali injection experiments. Oil analysis and phase behavior experiments were performed to find the origin of this improvement and to model the observed phase behavior using our new equation-of-state (EoS).

Oil analysis results show that the acids in crude oil are a complex mixture of various polar species and not mainly carboxylic acids. Phase behavior experiments show that the system does not undergo typical Winsor microemulsion behavior, but instead generates water-in-oil macroemulsions that are highly viscous. The key here is to form enough surfactants to generate reasonably low interfacial tension while keeping microemulsion viscosity below 10 cp.

Core flood recovery cannot be explained by the formation of a Winsor microemulsion phase, as is expected in surfactant EOR, largely because of the formation of these macroemulsions before such idealized phase behavior can occur. A substantial decrease in interfacial tension is observed in some cases without the formation of a viscous phase, although the IFT reduction occurs in a narrow window of alkali concentration and changes in other formulation variables. Corefloods perform well in this range, although the incremental recovery in some cases could be overestimated by solubility of water in these macroemulsions within the oil phase. The oil phase must be analyzed for its water concentration.

The peculiar viscous phase behavior can likely be explained by the presence of saltcrude complexes, created by acids from the crude oil under the alkali environment. These hydrophobic molecules tend to agglomerate at the oil-water interface altering the phase behavior. Together with polar components from the crude oil, they can organize into a highly viscous network and stabilize water droplets in the oleic phase. Oil-soluble alcohol is added to counter those two phenomena at large concentrations, but typical Winsor phase behavior is still not observed. A physicochemical model is proposed to capture the saltcrude complex formation and to explain the viscous phase formation at the oil-water interface.

The proposed surfactant generation mechanism will aid the design of pilot testing the alkali-cosolvent process for this specific oil but could also be applied to field implementation with other high TAN crudes. The formation of viscous phases caused by alkali is not discussed widely enough in the context of enhanced oil recovery in the literature, largely because formation of a viscous phase is quickly discarded as an incompatible surfactant system. However, alkali, as the main chemical for EOR, may be economic for some oils without the need to inject costly synthetic surfactants.

2.1 Introduction

After waterflooding, a significant amount of oil is trapped in the reservoir due to capillary forces. The trapped oil may be mobilized by reducing the interfacial tension between oil and water (Lake et al., 2014). The injection of alkali into an oil reservoir can reduce interfacial tension (IFT) between phases. IFT reduction is the result of in-situ soap generation (Ruding and Wasan 1992 a,b, Liu et al. 2008, Mohammadi et al. 2009). The saponification process includes multiple reaction steps where acid components from the crude oil partition into the brine phase. The acid components are then ionized in the brine phase to generate the soap (Chan and Yen, 1982). Alkali-surfactant-polymer (ASP) flooding is shown to recover additional oil after waterflood at both laboratory scale and field pilot tests at White Castle and West Kiehl fields (Clark et al., 1993, Falls et al., 1994, Shahin et al., 1996). Cosolvents have also been used in an alkali-cosolvent-polymer (ACP) process where cosolvents improve mobility, coalescence and shift phase behavior (Fortenberry et al. 2015).

Interfacial tension of the surfactant-oil-water system is correlated with the microemulsion phase behavior (Huh, 1979, Torrealba and Johns, 2017). In-situ generated soap in ASP flooding is expected to act as an anionic surfactant. Therefore, there is a need

for an accurate and predictive soap generation model and a microemulsion phase behavior model. Equilibrium of intermolecular forces between polar, nonpolar, and amphiphilic species govern microemulsion phase behavior types and transitions (Winsor, 1948). Four microemulsion phase behavior types are defined by Winsor (1948) based on equilibrated phases: type II- (water-rich microemulsion and excess oleic phases), type II+ (oil-rich microemulsion and aqueous phases), type III (microemulsion, aqueous, and oleic phases), and type IV (single microemulsion phase).

Both soap generation and alkali-crude oil phase behavior are complex phenomena that have been addressed in the literature. Petroleum acids may partition into the aqueous phase, where they dissociate to form soap molecules (de Zabala et al., 1982, Sharma and Yen, 1983). Several other important reactions involved in soap generation, including deactivated soap-salt complex (salt-crude complex hereafter) formation and partitioning of deactivated soap into oleic phase, were proposed in the literature (Chen and Yen, 1982, Ramakrishnan and Wassan, 1983). Crude oil may contain a mixture of complex components, such as asphaltenes, resins, petroleum acids, and alkanes. Acevedo et al. (1993) presented the formation of a highly viscous film between crude oil and water, which is sensitive to pH and salt.

Moreover, Horváth-Szabó et al. (2002) presented an optical study of liquid crystal phase formation, as a result of mixing oil, petroleum acids, and high pH alkali aqueous phase. A ternary mixture of water, toluene, and hydrocarbon acids may result in the simultaneous presence of multiple phases, such as liquid crystal, gel, microemulsion, aqueous, and oleic phases (Horváth-Szabó et al., 2001). Therefore, more complex phase behavior may be anticipated for enhanced oil recovery field applications, rather than initially expected interfacial tension reducing microemulsion phase behavior.

In this research, we made measurements of the phase behavior for various mixtures of alkali-alcohol-brine-OMV crude oil systems. We did not observe typical microemulsion phase behavior. As speculated here, we do not see Winsor phase behavior owing to the formation of salt-crude complexes. The results have been qualitatively matched using an updated soap generation model. First, we present a theoretical model for soap generation based on multiple reactions that are likely occurring. Second, we present experimental results from oil analysis, alcohol analysis, and phase behavior for the alkali-alcohol-brineoil system. Third, these results are then examined in light of the core flooding experiments conducted by HOT Microfluidics GmbH.

2.2 Model for soap generation

Owing to the complex nature of the crude oil, a more advanced soap generation model was developed based on previous literature for acidic crude oil interaction with alkali and salt aqueous solutions. The reactions are assumed to be at equilibrium.

An important first step in the process of soap generation is acid partitioning into the brine phase from the oil phase. Oil acid partitioning can be modeled using (de Zabala et al., 1982),

$$HA_{o} \rightleftharpoons HA_{w}$$
, $K_{D} = \frac{C_{HA_{w}}}{C_{HA}}$

where, HA_{w} is a non-dissociated aqueous acid, HA_{o} is a non-dissociated oleic acid, K_{D} is petroleum acid equilibrium constant. The acid then disassociates into the aqueous phase, which is governed by,

$$HA_{w} \rightleftharpoons H^{+} + A^{-}, \qquad K_{A} = \frac{C_{H^{+}}C_{A^{-}}}{C_{HA_{w}}},$$

where, A^- is active soap molar concentration, K_A is acid dissociation equilibrium constant. Water dissociation is important as well to calculate the pH. That is,

$$H_2 O \rightleftharpoons H^+ + O H^-, \qquad K_w = C_{H^+} C_{O H^-},$$

where, K_w is the water dissociation equilibrium constant.

Finally, an important overlooked reaction is soap deactivation by salt proposed by Chan and Yen (1982). Soap deactivation by salt cations may lead to counter-intuitive effects. Dissociated carbonate resulting from the addition of sodium carbonate increases the pH, which promotes acid partitioning into the aqueous phase. However, counter ion sodium concentration also increases, such that generated soap molecules are deactivated to create salt-crude complex, NaA.

$$NaA_{w} \rightleftharpoons Na^{+} + A^{-}, \qquad K_{1} = \frac{C_{Na^{+}}C_{A^{-}}}{C_{NaA_{-}}},$$

where, NaA_{w} is a salt-crude complex in the aqueous phase. Ramakrishnan and Wassan (1983) stated that due to the hydrophobic nature of petroleum acids, the salt-crude complex preferentially partitions back into the oleic phase:

$$NaA_{o} \rightleftharpoons NaA_{w}, \qquad K_{2} = \frac{C_{NaA_{w}}}{C_{NaA_{o}}} << 1$$

where, *NaA_o* is a salt-crude complex in oleic phase. The above reaction could be critical to the alkali-cosolvent-polymer process, owing to these salt-crude complexes causing the reduction of acid soaps and formation of a well-structured high viscosity phase (to be discussed later).

Therefore, combining the above two reactions yields (Ramakrishnan and Wassan, 1983),

$$NaA_{o} \rightleftharpoons Na^{+} + A^{-}, \qquad K_{D_{NaA}} = \frac{K_{1}}{K_{2}} = \frac{C_{Na^{+}}C_{A^{-}}}{C_{NaA_{o}}},$$

where, $K_{D_{NAA}}$ is salt-crude complex equilibrium constant.

Fig 2.1 illustrates the key reactions in the soap generation model. Added sodium carbonate alters the pH and sodium concentration in the aqueous phase. The soap generating hydrocarbon species may partition into the aqueous phase, but could also partition back into the oleic phase as a salt-crude complex. Soap generation requires species transfer between oleic and aqueous phases, so any barrier at the oil-water interface, such as a highly viscous layer, may prevent further soap generating reactions. The individual reactions used in this model are proposed in the literature. We use sodium carbonate as the alkali and solve the network of reactions. Ramakrishnan and Wassan (1983) have a similar solution for sodium hydroxide alkali, but they make certain simplifying assumptions. We solved the reaction network based on equilibrium constants without simplifying assumptions.

The amount of soap generated can be obtained by combining the reactions with a simple mass balance. A mass balance for the oil acidic component in the oleic and aqueous phases is:

$$S_{o}C_{HA}^{0} = S_{w}C_{HA_{w}} + S_{w}C_{A^{-}} + S_{o}C_{HA_{o}} + S_{o}C_{NaA_{o}},$$



Fig 2.1 Illustration of key reactions involved in the proposed soap generation model. Modified from Ramakrishnan and Wassan (1983), de Zabala et al. (1982), and Chan and Yen (1982).

where, S_o is oil saturation, S_w is water saturation. The use of equilibrium ratios gives an expression for generated natural surfactant (soap):

$$S_{o}C_{HA}^{0} = S_{w}\frac{C_{H^{+}}C_{A^{-}}}{K_{A}} + S_{w}C_{A^{-}} + S_{o}\frac{C_{H^{+}}C_{A^{-}}}{K_{A}K_{D}} + S_{o}\frac{C_{Na^{+}}C_{A^{-}}}{K_{D_{NaA}}},$$

or,

$$C_{A^{-}} = \frac{\frac{S_{o}}{S_{w}}C_{HA}^{0}}{1 + \frac{K_{w}}{K_{A}C_{OH^{-}}} \left(1 + \frac{S_{o}}{S_{w}K_{D}}\right) + \frac{S_{o}}{S_{w}}\frac{C_{Na^{+}}}{K_{D_{NaA}}}}.$$
(1)

where, all concentrations are expressed in [mol/l] units.

 C_{HA^0} is calculated based on Total Acid Number (TAN) of the crude oil, where TAN is the mass of KOH (in milligrams) required to neutralize one gram of oil. For example, no soap can be generated for zero TAN. C_{OH^-} is calculated from the molar concentration of Na_2CO_3 or NaOH, assuming that initial hydroxide concentration in water is negligible compared to added alkali. C_{Na^+} is a molar concentration that comes from both alkali Na_2CO_3 and salt NaCl.

The soap generation model depends on accurate equilibrium constants for the reactions and oil-water partitioning. We used equilibrium reaction constants from the literature, although they may vary greatly: $pK_A = 4.9$ based on carboxylic acids (Havre et al., 2003), which may differ due to the presence of various acidic species in the crude oil

as will be discussed in the later sections. Smith and Tanford (1973) demonstrated a linear relationship between carboxylic acid alkane chain length and pK_D in a water heptane system. Moreover, Havre et al. (2003) have shown a similar linear relationship for naphthenic acid with one, two, and three benzene rings for water crude oil phases. The presence of several benzene rings did not alter pK_D values of carboxylic acids significantly. In this project, we use a pK_D linear relationship from Havre et al. (2003) experimental data, assuming similar crude oil behavior $pK_D = 0.474n - 2.667$ (see Fig 2.2), where *n* is the number of methyl groups in the linear acid chain.

The physical implication of the trend in Fig 2.2 is that petroleum acids partition more into the oleic phase with increasing carbon tail length. The number of methyl groups n is a tuning parameter for modeling (Ghosh and Johns, 2018). The actual carboxylic acid in the crude oil has n = 16, as we will show in the next sections. However, there are other heavier polar components that may act like acids. Therefore, we use n = 22, as tuning parameter, which corresponds to a relatively large tail length for the acid to honor the highly oleic nature of the acid. The main unknown for a water-crude oil system is $K_{D_{Max}}$, an equilibrium constant that is expected to be unique for each species. $K_{D_{Max}}$ should be smaller for larger hydrophobic petroleum acids with larger n.


Fig 2.2 Crude oil acid partitioning coefficient between crude oil and water as a function of the number of methyl groups in a linear acid chain with one, two, and three benzene rings. Data from Havre et al. (2003).

In this project, we tuned $K_{D_{Max}}$ and demonstrated parameter sensitivity for soap generation. When we added sodium carbonate to increase the system pH, sodium ion concentration increased in the brine. The pH is calculated from the sodium carbonate concentration using a procedure outlined in Ghosh and Johns (2018). The Sharma and Yen (1983) model for soap generation for low sodium concentration would not be applicable for the sodium carbonate pH alteration, because adding sodium carbonate changes both pH and sodium concentration. Fig 2.3 illustrates soap generation based on the formation of the salt-crude complex.

Considering only pH alteration by sodium carbonate, such as in the Sharma and Yen (1983), model predicts more soap generation for higher sodium carbonate concentration. However, according to the proposed model, sodium ions created by sodium carbonate dissociation also deactivate soap molecules and forms an oil-soluble salt-crude complex. The expected Winsor type transition is illustrated based on phase behavior transition as a function of sodium concentration. The soap generation model will be compared with experimental results in later sections.

Fig 2.4 shows that more hydrophilic petroleum acid (larger $K_{D_{NaA}}$) generates more soap molecules. At the limiting case of infinite $K_{D_{NaA}}$, the salt-crude complex preferentially partitions into the aqueous phase rather than the oleic phase. The proposed model approaches the Sharma and Yen (1983) formulation that is insensitive to sodium concentration (see Eq. 1). Moreover, when $K_{D_{NaA}}$ is smaller, salt-crude complex preferentially partitions into the oleic phase, which generates a smaller amount of soap. In all cases, the amount of generated soap reaches a maximum value and then decreases owing to the reaction which consumes active soap to form a salt-crude complex at higher sodium concentrations. Before formation of any Winsor phase behavior surfactant may partition into oleic and/or water phases. Therefore, we may have surfactant generation that is *always* below critical micelle concentration, i.e. there is *not enough* surfactant to form any microemulsion phase behavior.

2.3 Experiments

We conducted a series of experiments to investigate the soap generation from petroleum acids. First, we analyzed crude oil composition via asphaltene precipitation, gas chromatography and mass spectrometry, and total acid number analysis. Second, we performed crude oil – alcohol – deionized water (DI) water phase behavior experiments to determine a phase diagram. Third, phase behavior is investigated via alkali scans, salinity scans, and alcohol scans (see Table 2.1). The experimental procedures are shown in Appendix A.



Fig 2.3 Soap generated as a function of sodium carbonate added. Winsor types are speculated here, not calculated or observed in the experiments. The above graph was generated for the following conditions: TAN is 2, n is 22, WOR is 1, oil density is 0.9 g/cc.



Fig 2.4 The sensitivity of soap generation model on $K_{D_{NaA}}$.

	Alkali	Salt	Alcohol	Remarks
Alkali scan	0 - 3.6% wt. Na ₂ CO ₃	Х	X	Fig 2.14
Alkali scan	0.2 - 2% wt. NaHCO ₃	X	X	Fig 2.19
Alkali scan	0.2 – 2% wt. NaOH	Х	х	Fig 2.19
Alkali scan	0.6 – 2% wt. KOH	Х	x	Fig 2.19
Salinity scan	4% wt. Na ₂ CO ₃	0 – 13.5% wt. NaCl	x	Fig 2.20
Alkali scan	0 - 3.6% wt. Na ₂ CO ₃	Х	11% vol	Fig 2.22
Alcohol scan	1.2% wt. Na ₂ CO ₃	Х	0 – 8.8% vol	Fig 2.23a
Alcohol scan	2.4% wt. Na ₂ CO ₃	Х	0 – 8.8% vol	Fig 2.23b
Salinity scan	4% wt. Na ₂ CO ₃	0 – 13.5% wt. NaCl	11% vol	Fig 2.25

Table 2.1 Experimental conditions for the phase behavior scans.

2.3.1 Oil analysis

This section provides results from the oil analysis experiments: Total Acid Number (TAN) and gas chromatography mass spectrometry (GCMS).

1.3.1.1 TAN analysis

TAN is measured according to the procedure outlined by Fan and Buckley (2006). KOH solution in isopropanol is used as a titrant (known concentration of KOH) for the experiment. A mixture of toluene-isopropanol-water with stearic acid and crude oil is used as a substance being analyzed. The electric potential of the solution was measured using a pH meter as titrant is added to the solution. Both blank and crude oil solutions are titrated to determine the inflection point of the electric potential and the added titrant amount are recorded.

The TAN is calculated according to

$$TAN = \frac{(V_i - V_b) \times M \times MW}{W} = \frac{(2.0 - 0.7)[ml] \times 0.05 \left[\frac{mol_{KOH}}{l}\right] \times 56.1 \left[\frac{g}{mol}\right]}{2.05[g_{oil}]} = 1.78 \left[\frac{mg_{KOH}}{g_{oil}}\right],$$

where V_b is the titrant volume at the base solution inflection point, V_i is the titrant volume at a sample inflection point, M is a molar concentration of potassium hydroxide, MW is a molar mass of potassium hydroxide, and W is the mass of sample oil. From Fig 2.5, TAN is 1.78 mg KOH/g oil, which is a large acid number that makes the OMV oil a potentially excellent choice for alkali flooding. TAN analysis indicates the abundance of acidic polar components. However, not all the acidic components in the crude oil can generate soap. Some acids can be part of complex polar oleic components that do not generate soap in the alkali solution. Moreover, Fan and Buckley (2006) and Purswani et al. (2017) state that TAN is not an accurate measure of the reactive compounds. Therefore, more analysis on oil composition is performed, as described next.



Fig 2.5 TAN analysis of OMV crude oil. 'OMV trials' represent titration experiments with crude oil (repeated three times), and 'base trials' represent titration experiments of blank solutions without crude oil (repeated three times).

1.3.1.2 GCMS analysis (crude oil, separated asphaltenes)

First, we removed asphaltene from the crude using the procedure described in Appendix A. Second, we performed the GCMS experiment on asphaltene free fraction of the oil. Third, we performed GCMS analysis on extracted asphaltene fraction.

Fig 2.6 shows the effluent time and amount of components detected at the outlet of the GC at specified times. Each species has its own time to travel through the chromatographic column. For example, lighter components exit the column at a shorter time scale, while larger molecules take more time to exit the column. Similar species travel together through the column, so peaks in intensity correspond to an affluent time of a certain component. The intensity peaks are then analyzed in mass spectrometry (MS).

Crude oil is a complex mixture of species. To isolate a particular component, intensity background is subtracted for each peak so that effluent noise from other species is reduced. We analyzed peaks to identify potential species in the crude to see what type of components and acids are present. The method cannot identify every species given the complex heterogeneous mixture of crude oil. Note that asphaltenes are already separated from the crude, and the species shown below are present only in the crude-pentane solution. Thus, there are heavier species that are not observed in the chromatogram.



Fig 2.6 Results from crude oil: x-axis is effluent time, and y-axis is relative intensity. See figure 1.7 for species identification.



Fig 2.7 Mass spectrometry analysis. Species identification is given as 'exit time [probability of specie identification]'. Potential species: A. 13.2 min [21%], B. 17.15 min [11.5%] C. 19.93 min [6.3%] D. 33.75 min [13.6%] E. 32.95 min [16.8%] F. 34.60 min [11%] G. 32.50 min [9.6%] H. 31.20 min [13%].

As can be seen from Fig 2.6 and Fig 2.7, there are plenty of large polar and nonpolar molecules available in the crude. Our objective was to identify polar carboxylic acids in the crude, so we conducted sample derivatization. Particularly, trimethylsilylether (TMS) is used as a derivatization agent. TMS replaces acid in the structure of the molecule so that the TMS component can be traced in the mass spectrometry. We also examined specific m/z cuts of the chromatogram to identify a derivative TMS group. Mass to charge ratio (m/z) is a functional group characteristic. TMS group has a characteristic m/z ratio of 73. From Fig 2.8 there are two distinct peaks with the derivative TMS group at times 22 and 24.2 min. The identified species are a soap generating oil component with a carboxylic group. However, the amount of soap generating species is not abundant, as indicated by no distinct peak at the total chromatogram in Fig 2.6. Therefore, there might not be enough soap generated to form the microemulsion phase for alkali-co-solvent-polymer enhanced oil recovery.

We further investigated the nature of the asphaltene precipitants. Due to high polarity of the precipitated components and presumably large molecular weight conventional GC columns cannot be used for heavy polar fraction components. Thus, a wax column is used instead. The analysis did not give any predominant species as a distinct peak. The following polar aromatic species are determined in the pentane insoluble oil fraction.



Fig 2.8 GC results from crude oil: x-axis is effluent time, and y-axis is relative intensity. See Fig. 1.10 for species identification.



Fig 2.9 Mass spectrometry analysis result. Species identification is given as 'exit time [probability of species identification]': 22 min [49.7%].



Fig 2.10 Mass spectrometry analysis of pentane insoluble crude oil fraction (asphaltenes) using wax column. Species identification is given as 'exit time [probability of species identification]'. Potential species: A. 9.93 min [77%], B. 12.1 min [10%] C. 8.75 min [24%] D. 9.8 min [27%]

There are other polar species in the oil; however, there are no distinctive peaks for individual species that can be detected. Moreover, large molecules have more possibility to form isomers. The above-identified species are referred to as resins, aromatic rings with polar functional groups. Resins and larger asphaltenes are known to form stable water emulsions in an oleic phase (Schorling et al., 1999), and not microemulsions, which are desired for enhanced oil recovery applications.

2.3.2 Alcohol-water-oil phase behavior

2.3.2.1 Phase diagram

We conducted phase behavior experiments that cover the entire compositional space for alcohol/DI water/crude oil system at fixed room temperature. The reason for this was to determine the nature of the alcohol and whether it partitions preferably in the oil or water. Ideally, cosolvent should partition between both the oleic and brine phases. It is observed that partitioning alcohol could be used to obtain favorable viscosity of microemulsion (Tagavifar et al., 2018). The alcohol is engineered by Clariant, and the exact chemical composition/structure is confidential.

From the phase behavior results, oil and alcohol are fully miscible throughout the binary alcohol-oil axis. Moreover, partial miscibility of water in alcohol is observed. That is about 3% vol. of water is soluble in alcohol, and <1% vol. of alcohol is soluble in water. If we treat alcohol as a pseudo surfactant, the alcohol demonstrates highly lipophilic

behavior (highly type II+). The entire compositional space can be seen in Fig 2.11, while the phase behavior experiments are shown in Fig 2.12. It is not clear that having an oilpartitioning alcohol is ideal.

One could recover more oil in the coreflood experiments by increasing the alcohol concentration, but this is not typically economical. Oil and pure alcohol are first-contact miscible. So, injecting a significant percentage of alcohol content by itself will yield to good recovery.



Fig 2.11 DI water (C1), crude oil (C2), and alcohol (C3) ternary phase diagram (volumetric composition).



Fig 2.12 a. Phase behavior along oil-alcohol axis (1.25, 5, 40, 60, 95, 98.75% vol. alcohol); b. Phase behavior along water-alcohol axis (1.25, 5, 40, 60, 95, 98.75% vol. alcohol); c. Phase behavior for constant water composition (2.5% vol) and varying oil-alcohol amounts (1.25, 5, 40, 60, 92.5, 95% vol. alcohol).

2.3.2.2 TAN with alcohol analysis

The same total acid number analysis is performed with oil mixed with alcohol. The analysis is performed to identify if alcohol may neutralize any of the petroleum acids. To perform the consistent analysis, we used the same amount of crude oil and tested the crude oil with and without alcohol. According to the definition of TAN, the mg KOH is used to neutralize crude oil and not crude oil with alcohol mixture. We used 2.05 g of oil and 0.5 g of alcohol for the analysis:

Fig 2.13 shows the TAN analysis results with alcohol. The experiments were repeated at least twice to ensure consistency and repeatability of the results. From the above, the presence of alcohol does not significantly change the acid number for a fixed amount of crude oil. However, as the crude oil is diluted with alcohol, the amount of acidic species in the oleic phase decreases, so the acid number decreases as well. The calculations are as follows:

If the oleic phase is 100% wt. oil:

$$TAN_{oileic \ phase: \ pure \ oil} = \frac{\left(V_i - V_b\right) \times M \times MW}{W} = \frac{\left(2.0 - 0.7\right) \left[ml\right] \times 0.05 \left[\frac{mol_{KOH}}{l}\right] \times 56.1 \left[\frac{g}{mol}\right]}{2.05 \left[g_{oil}\right]} = 1.78 \left[\frac{mg_{KOH}}{g_{oil}}\right]$$

If the oleic phase is 83% wt. oil, 17% wt. alcohol

TAN_{oileic phase: 83% w oil,17% w alcohol} =

$$= \frac{(V_i - V_b) \times M \times MW}{W} = \frac{(2.0 - 0.7)[ml] \times 0.05 \left[\frac{mol_{KOH}}{l}\right] / l \times 56.1 \left[\frac{g}{mol}\right]}{2.05 [g_{oil}] + 0.5 [g_{alcohol}]} = 1.43 \left[\frac{mg_{KOH}}{g_{oil_{mix}}}\right]$$

Thus, the addition of alcohol does not neutralize crude oil acids. However, the alcohol reduces the total acid number due to the dilution of oil components in the oleic phase.



Fig 2.13 TAN analysis of OMV crude oil with alcohol. 'OMV trials' represent repeated titration experiments with crude oil with and without alcohol, and 'base trials' represent repeated titration experiments of blank solutions without crude oil and alcohol.

2.3.3 Phase behavior experiments

2.3.3.1 Effect of alkali

Alkali scan (0% wt. salts, 0% v alcohol)

We first performed an alkali scan from 0 wt.to 3.6% wt.. sodium carbonate with no salt in the brine (see Fig 2.14). We observed that oil-brine mixtures undergo some phase behavior changes in phase compositions but not phase change. The results were not typical Winsor behavior.

At lower alkali concentrations (0.4 - 2.4% wt. sodium carbonate), the phase behavior is not a typical microemulsion phase behavior transition predicted by Sharma and Yen (1983) and the UTCHEM 9.0 (2000) soap generation model. We expected soap to be generated with increasing sodium carbonate concentration that would ensure type II-, III, II+ phase behavior transition. Instead, we see more complex phase behavior. The lower phase is predominantly water with some equilibrated dispersed oil (likely solubilized oil as microemulsions). The phase behavior appears to be type II- (equilibrium of excess oil with microemulsion), but it is not. This is evident by the observation that the upper phase volume is greater than the initially added oil volume. Thus, the upper phase is not pure excess oil and must contain a substantial amount of water, alcohol, and/or surfactant. The composition of the upper phase, as will be shown in section 3.4, is an oil with emulsified water (likely with soap component and salt-crude complexes). The upper phase is typically highly viscous (as is discussed later). Therefore, the phase behavior at concentrations from 0.4 - 2.4% wt. sodium carbonate is likely an equilibrium of microemulsion (lower) and macroemulsion (upper) phases. We diluted the lower phase using dichloromethane (DCM), which is miscible with water and immiscible with water. The oil from lower phase was not stripped by DCM, this means that dispersed oil is solubilized in water and lower phase must be a microemulsion.

At higher alkali concentrations (2.4 - 3.6% wt. sodium carbonate and up), a viscous gel-like layer is generated at the oil-water interface (>>10 cp). The presence of a highly viscous layer likely prevents equilibration of the mixture, so we cannot deduce the final equilibrated state. The viscous layer 'plugs' the interface between oil and alkali solution, whereas both water and oil are mobile in the pipette (see Fig 2.15). When the pipette is tilted to a nearly horizontal position the oil-argon interface spreads to maintain a flat horizontal interface; however, the viscous layer does not react to the tilt of the pipette indicating its highly viscous nature as shown in Fig 2.15. Argon is added at the top just before sealing the pipettes to ensure no contamination of air into the system.

The upper phase viscosity at low sodium carbonate concentration is highly viscous and shear thinning. The shear-dependence of the upper macroemulsion viscosity is shown in Fig 2.15. The viscosity measurements were done using the LS300 viscometer. The shear-dependent viscosity is especially important for the field scale applications, where shear rates vary significantly throughout the field, especially near wells. Moreover, large magnitude and shear-dependent viscosity implies complex structures and interactions in the upper macroemulsion phase. The complex structures at upper macroemulsion are being broken under high shear rate conditions.

One likely explanation of the complex alkali phase behavior observed is as follows. As alkali concentration increases, we generate soap molecules of various types in the aqueous phase (see A, B, and C in Fig 2.16a). The soap molecules solubilize the oil from the oleic phase. At the same time, salt-crude complexes are generated (see Fig 2.16b). Due to their hydrophobic nature, those salt-crude complexes transfer back to the oleic upper phase but agglomerate at the water-oil interface. The salt-crude complexes act as 'glue' that agglomerates with asphaltene and resin species identified in the crude oil (see Fig 2.9). Those glued polar agglomerates stabilize water droplets in the oleic phase as water-in-oil macroemulsions (see Fig 2.17). Similar water-in-oil emulsification mechanism is observed for asphaltene-resin rich crude oil (Mclean and Kilpatrick, 1997). However, for the alkali case, additional gluing components are represented as salt-crude NaA complexes. The polar agglomerates with water droplets then organize to form a well-structured network. Therefore, such an ordered network results in a shear-dependent highly viscous upper macroemulsion. The viscous layer likely slows down the reaction rate that happens at the oil-water interface where polar oleic components meet alkali in the aqueous phase to react (see Appendix B). It is known that pore size can affect phase behavior properties (Pitakbunkate et al., 2014), but in our research we do not consider pore size effects.



Fig 2.14 Alkali scan from 0% wt. to 3.6% wt. sodium carbonate.





Fig 2.15 Viscous interface viscosity analysis.



Fig 2.16 Results are generated by the proposed model shown in figure 1: a. active soap generation as a function of sodium carbonate concentration, CMC are shown for illustration purposes, typical CMC is around 10^{-3} to 10^{-2} mol/l (Rosen, 2004); b. fraction of original oleic acids converted into specified species as a function of sodium carbonate concentration.

a.



Fig 2.17 A potential mechanism for water in oil stable emulsion. The emulsion is stabilized by agglomeration of oil polar components and NaA salt-crude complexes. Modified from McLean and Kilpatrick (1997).

2.3.3.2 Effect of water-to-oil ratio

We conducted experiments to evaluate how the water-oil ratio (WOR) affects soap generation. WOR is an important parameter to consider in the oil recovery context because injected alkali water is in contact with reservoir oil at various saturation ratios during an ASP or ACP flood. More oil can be generated when the oil volume contacted is greater.

We prepared fixed sodium carbonate concentration aqueous solution (0.7% wt., 0% wt. salts) and mixed with crude oil at ratios from 5% aqueous saturation to 95% aqueous saturation. According to the experiments in Fig 2.18, the amount of soap that is generated qualitatively decreases with increasing WOR, because the brown lower phase becomes lighter brown as the WOR increases. The brown color of the lower phase represents oil that is solubilized by generated surfactant. The lower phase generates less soap and solubilizes less oleic components with increasing WOR. Our proposed soap generation model also predicts less soap generation at higher WORs (see Eq 1., page 15).



Fig 2.18 Water-oil ratio scan at fixed sodium carbonate concentration of 0.7% wt. Aqueous phase saturations scan as follows: 0.05, 0.10, 0.15, 0.20, 0.30, 0.70, 0.80, 0.85, 0.90, 0.95 (left to right).

2.3.3.3 Effect of alkali type

We investigate the impact of used alkali (sodium bicarbonate, potassium hydroxide, sodium hydroxide, sodium carbonate) on phase behavior in a specified range of alkali scan 0.2 - 2% wt.. The experiments are conducted at WOR of unity. We tried different types of alkali to see if we obtain Winsor type phase behavior.

Fig 2.19 shows the phase behavior of oil and alkali aqueous solutions using four types of alkali. The type of alkali impacts phase behavior. Sodium bicarbonate does not affect phase behavior under specified concentration range, i.e. initially mixed aqueous and oleic phases equilibrate to original phase volumes. Potassium hydroxide and sodium carbonate phase behaviors are similar in the specified range. According to our results, the lower phase (predominantly water) volume decreased, and upper phase (predominantly oil) solubilizes the water, as was shown in the previous sections. Literature suggests that alkali and crude oil mixture may lead to equilibration of the water-in-oil emulsion and the aqueous phase (Guo, 2006).

Sodium hydroxide phase behavior is similar to potassium hydroxide and sodium carbonate. However, sodium hydroxide is a stronger base, so more oil is solubilized in the water at lower concentrations. For example, at concentration of 0.6% wt. the lower phase is darker for sodium hydroxide compared to other alkali. Moreover, sodium bicarbonate did not show any solubilization of oil in the lower phase, implying no soap generation. This set of experiments indicates the sensitivity of the soap generation on the choice of alkali

type. Therefore, the recommended injection concentration ranges should be reconsidered from one alkali type to another. If one changes the alkali type for soap generation, then the target concentration will change from one alkali type to another.



Fig 2.19 Alkali scan phase behavior of crude oil and alkali aqueous solutions 0.2 - 2% wt. with a 0.2% wt. increment: a. sodium bicarbonate, b. potassium hydroxide, c. sodium hydroxide, d. sodium carbonate.

2.3.3.4 Effect of salt

Salinity scan (4% sodium carbonate, 0% v alcohol)

We fixed the alkali amount in each pipette and varied salinity to see the effect on phase behavior. We selected a relatively high alkali concentration to ensure an excess of alkali to react with acids in the oil (4% wt. sodium carbonate). We conducted a salinity scan from 0% wt. to 12% wt. of NaCl (see Fig 2.20a). The results show that the oil has a strong affinity to the glass surface in the aqueous environment, namely oil drops attach to the pipette surface (even after weeks). All samples formed a viscous layer at the water-oil interface (see Fig 2.20b). Moreover, the salinity scan did not affect phase behavior, likely indicating that the amount of soap generated is significantly less than the amount of saltcrude NaA complex.

As discussed previously, adding salt to the system may enhance the salt-crude complex generation and reduce the amount of active soap. According to our model, about 80% of total oleic acids convert into salt-crude complexes instead of generating active soap (Fig 2.21). Moreover, adding salt would decrease active soap generation and increase the amount of NaA formation.

According to OMV formation water analysis, the ion concentration of the brine is 1.9% wt. salt content. Depending on the K_{DNAA} equilibrium constant, the oil acids may form salt-crude complexes instead of expected active soap at such a salinity level. Moreover, other reactions are possible due to the presence of various ions in formation water, such as

sodium, calcium, magnesium, sulfate, ammonium, barium, strontium, and more. Those ions in the aqueous phase may potentially react with crude oil species and form other polar complexes. It may be possible to conduct a low alkaline concentration and low salinity flood and avoid the gel-like structures, but the interfacial tensions may not be low enough for the flood to be economical.



Fig 2.20 a. Salinity scan from 0% wt. to 13.5% wt. sodium chloride with an increment of 1.5% wt. (fixed 4% wt. sodium carbonate); b. the viscous layer is present between the water-oil interface.



Fig 2.21 Results are generated by the proposed model. A. active soap generation as a function of sodium chloride concentration, with fixed sodium carbonate at 4% wt. B. fraction of original oleic acids converted into specified species as a function of sodium chloride concentration, with fixed sodium carbonate 4% wt.

А

2.3.3.5 Effect of alcohol

Alkali scan with alcohol (0% wt. salts, 11% vol. alcohol)

Next, we performed experiments with alcohol to improve coalescence and to see if we achieve typical Winsor phase behavior. We first identified the alcohol solubility and affinity to oil or water (see the ternary diagram in Fig 2.11), where alcohol is fully miscible with oil and almost immiscible with water, implying the hydrophobic nature of the alcohol. We selected an overall alcohol volume fraction of 11% vol. to explore a limiting case of high alcohol content. However, experiments with lower alcohol content are also done as presented in the following sections. The alkali scan is from 0 to 3.6% wt. sodium carbonate at fixed alcohol concentration, as shown in Fig 2.22.

The main effect of alcohol is that it prevents viscous layer formation at the wateroil interface. That is, the viscous layer shown in Fig 2.15 and Fig 2.20b does not form at large alcohol concentrations. Moreover, soap generation is influenced by alcohol, as seen by comparing Fig 2.14 (without alcohol) and Fig 2.22 (with alcohol). For alkali concentrations from 0.4 to 2.4% wt. without alcohol, the lower phase (microemulsion) contains dispersed oil. For alkali concentrations of 0 to 0.4 % wt. *with alcohol*, the lower phase also contains some oil. For higher concentrations, however, no oil solubilization is observed.

No viscous condensed phase is observed in the presence of alcohol at any alkali concentration for these high alcohol concentrations. Fig 2.23 shows that the minimum alcohol requirement is about 4.4% vol. to avoid the viscous layer. We confirmed the absence of the viscous layer by tilting the pipettes and flowing the phases. Fig 2.23 also shows that the amount of dispersed oil in the aqueous phase reduces with increasing alcohol content, likely suggesting less amount of soap being generated. Therefore, adding alcohol not only prevents viscous layer generation but also limits soap generation.

We hypothesize the following explanation of the effect of alcohol on phase behavior. As discussed previously, alcohol is soluble in oil and does not react (neutralize) oleic acids based on TAN analysis, see Fig 2.13 and Fig 2.11, respectively. Added alcohol likely solubilizes polar oleic components in the oil owing to its preference for the oleic phase. Both alcohol and polar acidic oil components have some surface-active characteristics. However, it is likely that alcohol preferentially occupies the oil-water interface over-acidic oleic components. Without alcohol, polar acidic components would be able to access the oil-water interface and generate soap. With alcohol though, the acidic polar species are less likely to reach the interface and thus, a smaller amount of acids have a chance to react with the alkali solution. Therefore, less soap is generated when alcohol is added to the system. We can also confirm the hypothesis based on Fig 2.23, where added alcohol reduces the amount of dispersed oil in the lower phase.

The alcohol solubilization of polar oleic components likely prevents the gluing of polar components around emulsified water (see Fig 2.24). Instead of the well-structured highly viscous layer at the interface, we get dispersed polar components in the oleic phase. Low alcohol content (2.2% vol. and less from our experiments, see Fig 2.23) does not
prevent viscous layer formation, i.e. the amount of alcohol is not enough to solubilize all oleic polar components, and therefore the viscous layer happens with alcohol as well. The abundance of polar species in the oleic phase is also observed when polar species responds to the presence of an electric field (see Appendix C).



Fig 2.22 Alkali scan 0% wt. to 3.6% wt. sodium carbonate (increment of 0.4% wt.) with fixed 11% vol. alcohol content.



Fig 2.23 Alcohol scan from 0% v to 8.8% v alcohol in the oleic phase (a. fixed 1.2% wt. alkali, b. 2.4% wt. alkali).



Fig 2.24 Proposed mechanism of alcohol effect on the gel and stable emulsion formation in oleic phase.

Salinity scan (1.6% wt. fixed alkali, 11% v fixed alcohol)

We next investigated the effect of salinity on the phase behavior of crude oil with alcohol. Salinity scans are performed with equal volumes of oleic (oil and alcohol) and aqueous (water and salt and alkali) phases. Alcohol overall volumetric concentration was 11% v, and alkali was 1.6% wt. in the aqueous solution for all pipettes. Salinity is varied from 0.1 to 13.5% wt. of NaCl in the aqueous solution.

The results show that salinity did not affect the phase behavior of the mixture (see Fig 2.25). Similar to the results in Fig 2.22, no gel-like viscous fluid is formed at the interface between brine and oil owing to the high alcohol content.



Fig 2.25 Salinity scan from 0.1% wt. to 13.5% wt. sodium chloride (fixed 1.6% wt. alkali, 11% v alcohol)

2.3.4 Coreflood analysis

2.3.4.1 Interfacial tension measurements

We qualitatively measured interfacial tension between oleic and aqueous phases using the Rame-hart 260 tensiometer using the crude oil and various alkali concentrations in the aqueous phase. The interfacial tension was significantly affected by the alkalinity of the aqueous phase (Fig 2.26). The interfacial tension is greatest when the aqueous phase is acidic, i.e., 0.37% wt. HCl. We tried the acidic solution to see the trend of interfacial tension as a function of alkalinity. Under acidic conditions, the acidic components in the oleic phase do not partition into the aqueous phase. Therefore, there is no generated soap.

The interfacial tension first reduces with increasing alkalinity of the aqueous phase (see Fig 2.26). The lowest interfacial tension measured is likely below 1×10^{-5} N/m (for 1 g/l to 10 g/l sodium carbonate), although the analysis was unclear owing to the drop shape. Such low interfacial tensions (three orders of magnitude lower) may explain additional oil recovery in the coreflood experiments when alkali is injected. However, no Winsor like microemulsion phase behavior is observed at 1 g/l concentration. Phase behavior experiments indicated that over time, a viscous layer forms around 1 g/l sodium carbonate conditions (around 0.1% wt.). Therefore, crude oil and alkali interactions are more complex here. At high sodium carbonate concentration (100 g/l) the interfacial tension increases again. Thus, an alkaline concentration of 4 g/l likely gives the lowest IFT. The coreflood used 7 g/l alkali concentration, which is the least amount of alkali needed to result in

significant changes in IFT (three orders of magnitude). The arrows in Fig 2.26 indicate that the IFT must be lower than could be analyzed with more precise tensiometer equipment.



Fig 2.26 The interfacial tension between oleic and aqueous phases as a function of aqueous phase basicity: dashed line represents the detectable limit of the equipment; arrows show the interfacial tensions that are lower than the detectable limit.

2.3.4.2 Experiments by HOT Microfluidics GmbH

Corefloods conducted by HOT Microfluidics GmbH demonstrate that injection of alkali chemical slug recovers a significant amount of oil – up to 41% of OOIP after water flooding (see Fig 2.27). The chemical slug contains sodium carbonate, sodium bicarbonate, sodium chloride, Clariant alcohol, and Flopaam 3630 S polymer. Injection of the similar chemical slug with polymer and salts, but without alcohol and alkali, did not produce significant additional oil recovery. The additional oil recovery is, therefore, attributed to the presence of alkali in the injected fluid.

It is likely, however, that improved oil recovery estimates are overestimated based on the phase behavior results presented in this report. Phase behavior experiments show that for the injection conditions used, the upper phase becomes a swollen macroemulsion phase (see Fig 2.28). The upper phase saturation increases from 0.5 to 0.9, likely because of a significant amount of dispersed water in the oil macroemulsion. The coreflood recovery is measured by the visual metering of effluent fluids. Swollen upper phase visually looks like the oleic phase, and could, therefore, be misinterpreted as oil recovery.

We have repeated the experiments using the chemical composition shown in the green box in Fig 2.28. The amount of emulsified water in the oleic phase varied from 5% up to 50% after two weeks of equilibration. The reason for such inconsistency is the fact that samples are not fully equilibrating in two weeks due to the presence of a viscous

interface that slows down the process. However, water is consistently emulsified in the oleic phase.

It is likely that the IOR due to alkali and alcohol injection are caused by the reduction of interfacial tension, by approximately three orders of magnitude. Other recovery mechanisms are possible, such as by wettability alteration, but this is not examined here.

Phase behavior of the crude oil diluted with cyclohexane and alcohol is sensitive to salinity (see Fig 2.28). All samples formed viscous layers close to the phase interface with varying viscosities. For example, phases under 1.2 - 2.1 % wt. salinity had a less viscous interface compared to other samples. However, the viscosity of those samples was still high compared to oil and water viscosity.

We do observe significant pressure drop change of one order of magnitude for the coreflood experiment when the chemical slug is introduced to the system (see Fig 2.27). However, the pressure drop increase is likely caused by the polymer in the chemical slug that increases the viscosity of the injected fluid. The chemical slug viscosity is about an order of magnitude higher than formation water, which explains the order of magnitude change in the pressure drop. Moreover, as we recover the oil bank, the pressure drop remains almost constant with an injected chemical slug. The viscosity of a viscous interface is highly shear-dependent and could still flow under coreflood shear rates. Coreflood shear rate is about 1s⁻¹. For pure oil the rate corresponded to 1400 cp, but with cyclohexane

dilution, the viscosity of the oleic phase is even lower, and likely the phase becomes recoverable. The key here is to lower interfacial tension as much as possible before a viscous phase occurs.

Interfacial tension reduction from DI to alkali solution is about three orders of magnitude. Such reduction is likely enough to alter the capillary number to recover additional oil, based on coreflood experiments. Based on the possible "overestimated" oil recoveries by HOT Microfluidics, we constructed a capillary-desaturation-curve (CDC) shown in Fig 2.29. We use flow irreducible oil saturations, flowrates, and viscosities from HOT Microfluidics experiment description sheet and IFT data based on Rame-hart tensiometer measurements. We see that the general trend follows the expected trend for the CDC curve mentioned in Fig. 1. Moreover, the reduction of the interfacial tension is sufficient to mobilize a portion of trapped oil, but not low enough to recover all of the trapped oil. The CDC curve is wetting-state dependent, therefore not universal. For OMV coreflood experiments aqueous phase composition was altered from the formation water to the chemical slug. Such alteration of composition could also cause wettability alteration of the rock and impact the shape of the CDC curve.



Fig 2.27 Oil recovery profile and pressure differential during chemical flooding experiments (Schumi et al., 2019). FW is formation water (18.96 g/l NaCl, 1.85 g/l NaHCO₃), CHEM is chemical slug (18.96 g/l NaCl, 1.85 g/l NaHCO₃, 7 g/l Na₂CO₃, 2 g/l alcohol, 2 g/l Flopaam 3630 S polymer). High flowrates (x5/x10/x5) were used with FW to test the true residual oil saturation.



Fig 2.28 Salinity scan (0.3, 0.6, 0.9, 1.2, 1.5, 1.8, 2.1, 2.4, 2.7, 3.0 in percent weight of NaCl) with crude oil (15%v cyclohexane, 0.1%v alcohol). The aqueous phase is 1.85 g/l NaHCO3, 7g/l Na2CO3, and varying salinity. The green line is the initial phase interface before mixing (WOR=1), the red line is phase interface after two weeks, blue rectangle is for OMV coreflood condition 1.8% wt. NaCl.



Fig 2.29 Capillary desaturation curve for HOT Microfluidics experiments using crude oil and chemicals.

2.4 Chapter 2 conclusions

The primary aim of the research is to characterize and model phase behavior of alkali/crude oil system using crude and chemicals. Oil recovery occurs under two-phase flow conditions, where some of the trapped oil is mobilized through IFT reduction. However, the recovery is not directly related to typical Winsor type phase behavior. Recoveries from the core flood experiments could be slightly overestimated owing to the swollen upper phase with water macroemulsions. The following conclusions are made:

- The improved oil recovery is evident via coreflood alkali injection experiments. The main cause of additional oil recovery is likely interfacial tension (IFT) reduction. The coreflood incremental recovery, in some cases, could be overestimated by the solubility of water in these macroemulsions within the oil phase.
- 2. We recommend sodium carbonate concentrations above 1g/l be used based on IFT measurements. Alcohol solubilizes polar oleic species and prevents the formation of the viscous phase. Alcohol concentrations to avoid the viscous layer at unity WOR is 4.4% by volume.
- 3. The phase behavior experiments do not undergo typical Winsor microemulsion behavior. Moreover, the experiments have shown more complicated behavior, such as the formation of viscous upper macroemulsion phase and viscous layer at the oilwater interface.

- 4. Oil analysis has shown the presence of various polar species instead of just carboxylic acids. The polar species under alkali environment likely form salt-crude complexes that potentially agglomerate into well-organized viscous networks at the oil-water interface. Moreover, the salt-crude complexes stabilize dispersed water droplets in oil and form viscous upper macroemulsion phase.
- 5. We proposed a reaction network that captures the salt-crude complex formation and explains viscous layer formation at the oil-water interface.
- 6. Coreflood results show great potential to use alkali based chemical slugs to improve the oil recovery, where the oil has acidic components.

2.5 Chapter 2 nomenclature

A^-	Active soap molar concentration
S_{o}	Oil saturation
S_w	Water saturation
C_i	Component <i>i</i> concentration
HA_{w}	Non-dissociated aqueous acid
HA_o	Non-dissociated oleic acid
NaA_{w}	Salt-crude complex in aqueous phase
NaA _o	Salt-crude complex in oleic phase
K_w	Water dissociation equilibrium constant
K_A	Acid dissociation equilibrium constant
K_D	Petroleum acid equilibrium constant
$K_{D_{Net}}$	Salt-crude complex equilibrium constant.
TAN	Total acid number

Chapter 3 Inclusion of Variable Characteristic Length in Microemulsion Flash Calculations

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Chapter Summary

Recent developments in predicting microemulsion phase behavior for use in chemical flooding are based on the hydrophilic-lipophilic deviation (HLD) and net-average curvature (NAC) equation-of-state (EoS). The most advanced version of the HLD-NAC EoS assumes that the three-phase micelle characteristic length is constant as parameters like salinity and temperature vary. In this chapter, we relax this assumption to improve the accuracy and thermodynamic consistency of these flash calculations.

We introduce a variable characteristic length in the three-phase region based on experimental data that is monotonic with salinity or other formulation variables, such as temperature and pressure. The characteristic length at the boundary of the three-phase region is then used for flash calculations in the two-phase lobes for Winsor type II-/II+. The functional form of the characteristic length is made consistent with the Gibbs phase rule.

The improved EoS can capture asymmetric phase behavior data around the optimum, whereas current HLD-NAC based models cannot. The variable characteristic

length formulation also resolves the thermodynamic inconsistency of existing phase behavior models that give multiple solutions for the optimum. We show from experimental data and theory that the inverse of the characteristic length varies linearly with formulation variables. This important result means that it is easy to predict the characteristic length in the three-phase region, which also improves the estimation of surrounding two-phase lobes. This improved physical understanding of microemulsion phase behavior should greatly aid in the design of surfactant blends and improve recovery predictions in a chemical flooding simulator.

3.1 Introduction

Surfactants serve various industrial purposes, including pharmaceutics, detergents, flotation agents for mineral extraction, and for enhanced oil recovery in petroleum engineering (Rosen, 2004). A mixture of surfactant, water, and an organic compound may result in complex microemulsion phase behavior (Winsor, 1948). Depending on the applications, the surfactants are designed to possess desired properties, such as salt tolerance, foaming, and low interfacial tensions (Rosen, 2004, Bourrel and Schechter, 2010). For petroleum engineering applications, surfactant slugs are injected to achieve ultra-low interfacial tension between the microemulsion phase and the excess oil and brine phases (Healy and Reed, 1976). At the laboratory scale, surfactant flooding experiments can recover nearly all residual oil in the core (Camilleri et al., 1987), which makes this technique potentially attractive for field applications.

Microemulsion phase behavior is addressed in the literature from various physicochemical perspectives. The phase behavior types and transitions are governed by intermolecular forces between polar, nonpolar, and amphiphilic species (Winsor, 1948). Four microemulsion phase behavior types were defined by Winsor (1948): type II- (waterrich microemulsion and excess oleic phases), type II+ (oil-rich microemulsion and aqueous phases), type III (microemulsion, aqueous, and oleic phases), and type IV (single microemulsion phase). Surfactants were classified in terms of a balance between hydrophilic and lipophilic structural groups (Griffin, 1949). Phase behavior transitions are observed in terms of formulation variables, such as temperature, pressure, salinity, alcohol content, oil type, and surfactant structure (Healy and Reed, 1976, Skauge and Fotland, 1990).

Surfactant is a complex species with hydrophobic and hydrophilic features that cause micelle formation. Micelle curvature is affected by the chemical potential of a surfactant molecule, and can be expressed by a characteristic length ξ defined originally by De Gennes and Taupin (1982). There are several definitions of characteristic length proposed in the literature. De Gennes and Taupin (1982) defined 'persistence length' as the distance at which the curvature of the surfactant layer can be assumed flat. Strey (1994) defined 'mean curvature' as the square root of the sum of the principal curvatures of a surfactant layer interface in the microemulsion phase. Acosta et al. (2003) defined 'average curvature' as the average of the inverse volumetric solubilization of oil and water in the microemulsion phase. The characteristic length therefore is a maximum length scale under

which oil/water/surfactant emulsion remains a stable single-phase mixture. For mixtures with a characteristic length larger than the maximum, single-phase mixtures become unstable and excess phases may form.

Several authors proposed microemulsion phase behavior models in the literature. For example, Gibbs free energy was expressed via modified Flory-Huggins theory to model microemulsion phase behavior qualitatively (Rossen et al., 1982, Kilpatrick et al., 1985). Phase behavior was also addressed using statistical thermodynamics modeling of the pseudo-ternary system on the lattice by assigning interaction parameters (Widom, 1986). The models capture general trends and can fit experimental data; however, it is difficult in practice to measure physical parameters for such models. Furthermore, they are generally not predictive away from tuned data.

For enhanced oil recovery, the modified Hand's model (Hand, 1930) is used to model two-phase lobes, while the three-phase invariant point (microemulsion composition) is modeled empirically based on limited experimental data (Pope and Nelson, 1978). Although a significant advance, a fully empirical approach such as this likely leads to poor predictions away from the measured data.

Salager et al. (1979) proposed a correlation for optimum three-phase zone estimation of surfactant/water/oil system in terms of temperature, salinity, oil type, alcohol content, and surfactant structure. Later, the concept was defined as the hydrophilic-lipophilic deviation (HLD) based on the surfactant chemical potential difference in the

oleic and aqueous phases (Salager et al., 2000). HLD, which is an intrinsic parameter related to the surfactant partitioning between the excess phases, is not sufficient to model phase behavior when the degrees of freedom are larger than one.

Acosta et al. (2003) combined HLD and average micellar curvature of both oil and water to make flash calculations in the three-phase region where only salinity varies (HLD-NAC). For such a system, the degrees of freedom $(2 + N_c - N_p)$ are three because there are four components (oil, water, surfactant, and salt giving $N_c = 4$) and three phases ($N_p = 3$). To make the calculation possible, Acosta and co-workers specified the salinity (to determine the brine pseudocomponent), HLD (surfactant partitioning K-value), and the maximum value of the characteristic length for the micelles. They assumed that the characteristic length in the three-phase region is fixed and equal to its maximum as salinity varies. The assumption of a constant characteristic length, however, causes the three-phase region to be symmetric around the optimum. Further, the two-phase regions were not modelled, except by application of "catastrophe theory," which leads to discontinuities in tie lines. Moreover, their approach did not vary the optimum solubility (or characterization length at optimum) with changing conditions such as temperature and pressure.

Ghosh and Johns (2016a) improved the Acosta model by developing a correlation for optimum solubilization ratio (optimum characteristic length) as other parameters change such as the equivalent oil alkane number (EACN). The flash calculation using the HLD-NAC equations were made dimensionless by Ghosh and Johns (2016b), which introduced the *I*-ratio. These improvements allowed for more accurate and predictive three-phase flash calculations and reduced the number of tuning parameters. However, the HLD-NAC model could still not physically model the two-phase lobes.

Khorsandi and Johns (2016) made significant practical advancements of the HLD-NAC based model to calculate the compositions of both the three-phase regions (tie triangles) and continuous two-phase lobes (tie lines) as formulation parameters like salinity, temperature, pressure, and EACN varied. In their dimensionless equation-of-state (EoS), they defined a critical tie-line condition for the two-phase lobes to calculate without iteration the tangent (limiting tie line) to the critical point. They also introduced a tie-line parameter to model tie lines within the two-phase lobes. They showed that each tie line has a unique characteristic length from which one could calculate the microemulsion phase composition. Their improved model, however, relied on the assumption that the characteristic length is constant in the three-phase region, making predictions less accurate.

In this chapter, we make a significant advance in flash calculation accuracy for the three-phase regions, and hence, the two-phase regions. We use a variable characteristic length in the three-phase region that is a function of all formulation variables. Such an improvement ensures thermodynamic consistency and allows asymmetric phase behavior around the optimum. We then update the Khorsandi and Johns (2016) flash calculation algorithm for a variable characteristic length and demonstrate its excellent ability to match experimental data.

3.2 Methodology

This section describes the model assumptions, the development of the variable characteristic length, and its implementation into an HLD-NAC equation-of-state algorithm.

3.2.1 Model assumptions and limitations

There are two primary independent thermodynamic properties of surfactant that govern microemulsion phase behavior: surfactant capacity to stabilize oil/water (described by the characteristic length) and surfactant affinity (hydrophilic-lipophilic difference or HLD). The characteristic length is a thermodynamic property; for example, in polymer science, the characteristic length of a polymer is a function of molecular interactions, governed by temperature and molecular structure (Rubinstein and Colby, 2003). The characteristic length therefore is an intensive property (Sandler, 2006).

The microemulsion phase is assumed to be packed with hypothetical spheres of radius:

$$R_i = \frac{3V_i}{A_s} = 3IL\sigma_i,$$

where, R_i is a hypothetical radius of oil or water domains, V_i is the volume of component *i* in the microemulsion phase, A_s is the area of the interface between oil and water domains

(micelles) within the microemulsion phase, $I = V_s / (A_s L)$ is the dimensionless surfactant interfacial volume ratio, *L* is the surfactant tail length, and σ_i is the solubilization ratio for component *i* (ratio of component *i* volume, V_i , to surfactant volume V_s in the microemulsion phase). The tuning parameter, *I*, is assumed constant. More details on these parameters and other assumptions can be found in Acosta et al. (2003), Ghosh and Johns (2016a), and Khorsandi and Johns (2016).

The fraction of oil or water within the microemulsion phase is controlled by the surfactant affinity (surfactant partitioning between the excess oil and brine phases) as expressed through the hydrophilic-lipophilic difference (HLD). For example, with varying salinity and temperature, $HLD = \ln K_s^{ow} = \ln S / S_{ref} - \alpha (T - T_{ref})$ where the reference state is one of the optimums, i.e. $(S,T)_{ref} = (S^*,T^*)$ where the asterisk indicates optimum conditions. At optimum, HLD is defined to be zero, which means that K_s^{ow} is assumed 1.0 there. Ideally, the exact value of the K-value would be measured at the reference optimum. See Khorsandi and Johns (2016) for more details regarding HLD.

3.2.2 Variable Characteristic Length

In this chapter, we use the Acosta et al. (2003) definition of characteristic length based on oil and water solubility represented through spherical micelles. A large characteristic length means that *more* oil and/or water can be stabilized in the microemulsion phase. A small characteristic length implies a poor ability to stabilize oil and water domains within the microemulsion phase.

The characteristic length is defined by Acosta et al. as the average curvatures of oil and water hypothetical spheres in both the two- and three-phase regions as,

$$\frac{1}{\xi} = \frac{1}{2} \left(\frac{1}{R_o} + \frac{1}{R_w} \right) ,$$
 (1)

where $\xi = \xi^{\text{max}}$ is assumed constant in the three-phase region. The three-phase dimensionless characteristic length $\xi_D^{3\phi} = \xi / L$ is then defined by the solubilities as (Ghosh and Johns, 2016b),

$$\frac{3I}{\xi_D^{3\phi}} = \frac{1}{2} \left(\frac{1}{\sigma_o} + \frac{1}{\sigma_w} \right) \,. \tag{2}$$

The constant value of 3*I* in Eq. (2) is retained on the left-hand side for convenience. At any optimum in formulation space we then have ($\sigma_o = \sigma_w = \sigma^*$),

$$\frac{3I}{\xi_D^{3\phi}} = \frac{1}{\sigma^*} \ . \tag{3}$$

For a constant optimum solubility, the optimum could then be determined by the harmonic mean for any point where three-phase solubilities are measured, whether at the optimum or not (Ghosh and Johns, 2016b). That is, $2/\sigma^* = 1/\sigma_o + 1/\sigma_w$ by equating Eqs (2) and (3).

Ghosh and Johns (2016a) showed that the inverse of the optimum solubility (or characteristic length) is linearly related to changing formulation variables such as EACN. Khorsandi and Johns (2016) later extended and formalized this relationship to include other variables, such as temperature and pressure. For example for varying temperature and pressure, they calculated the value for the constant characteristic length in the three-phase region (based on optimum) by $1/\xi_D^{3\phi} = \beta_1 T^* + \beta_2 P^* + \beta_3$, where there are three β_i tuning parameters, and (T^*, P^*) are at optimum.

Fig 3.1 illustrates the problem with using a constant characteristic length in the three-phase region. Possible micellar configurations are illustrated in the three-phase region, where oil and water become bi-continuous (Strey, 1994, Davis, 1994). Far from optimum, in type II- and II+ regions, micelles are more spherical. The characteristic pattern within the bi-continuous region is illustrated by rectangles in Figs. 1a, b, and c, where repeating this pattern generates all micelles in the microemulsion phase. Shown in the corresponding Figs. 1d, e, and f is the volume of hypothetical spheres of oil and water, needed to give the same volume as that in each rectangle. As shown, the droplets of oil and water at optimum are the same size (same solubilities in Fig. 1b, e), while in Fig 3.1a,

d (under optimum) the water droplet is significantly larger than the oil. Fig 3.1c, f show the over optimum case where the hypothetical oil volume in the droplet is larger than water. The surfactant volume is constant for all cases as surfactant is only in the microemulsion phase, which is assumed evenly distributed. These hypothetical droplets and their relative sizes form the basis of solubility calculations in the Acosta model (see Eq. (1)).

The optimum condition illustrated in Fig. 1 is one of many possible optimums in formulation space where for example EACN, salinity, T, and P can change. The characteristic length in Fig. 1 is constant in the three-phase region as evidenced by the same size, but reversed oil and water droplet in Fig. 1d and f. That is, the sum of the curvatures is identical because the values of the curvatures are simply interchanged.

There is no reason to believe, however, that the sum of the curvatures is equal as salinity changes (or other formulation variables) within the three-phase region. The salinity in Fig. 1a is smaller than the salinity in Fig. 1c, which means the brine pseudocomponent has changed and therefore the equilibrium state must be different. For small three-phase regions this could be a reasonable approximation, but not for three-phase regions that exist over a large change in formulation variables.

Fig 3.2 illustrates the potential significant shift in the optimum solubility where only temperature and pressure vary (salinity and EACN are fixed). Here we see an optimum locus that represents all possible optimums in T and P space. (An optimum locus is similar to a critical locus for vapor-liquid systems). Not all optimums are equal in that

the optimum characteristic length changes along this locus. Thus, some optimums will have higher or lower interfacial tensions as well (Huh, 1979). Consider point (T_1, P_1) that is not at an optimum. At constant pressure, the temperature can be increased (during a temperature scan) until optimum is obtained where solubilities are equal. The value of the characteristic length at this optimum (T_2^*, P_1^*) is given by $(3I / \xi_D^*)_1$ in Fig. 2. Even though pressure is fixed in this scan, the pressure is now at an optimum as indicated by the asterisk. Alternatively, pressure could be increased at a constant temperature until another optimum is reached at (T_1^*, P_2^*) where the value of the characteristic length is given by $(3I / \xi_D^*)_2$. These two values of the dimensionless characteristic length will likely be significantly different.

The equation used by Ghosh and Johns (2016) and Khorsandi and Johns (2016) to determine the optimum solubility, however, is thermodynamically inconsistent with the illustration in Fig. 2. For example, Khorsandi and Johns use $1/\xi_D^{3\phi} = 1/\xi_D^* = \beta_1 T^* + \beta_2 P^* + \beta_3$, but after tuning of the three constant coefficients, this expression will produce a different value of the characteristic length at the two optimums in Fig. 2 instead of a constant value. This inconsistency can cause significant errors in the phase behavior prediction for large changes in temperature, pressure, and EACN.

The characteristic length not only changes along the optimum locus, but therefore must also change for any values of the formulation variables within the three-phase region. Consider pressure scans at three fixed temperatures shown in **Fig 3.3**. The optimums for

each pressure scan are shown by the circles, where each has a different characteristic length as indicated by the optimum values, (see Eq. (3)). Assuming a constant characteristic length would give a significant error in this case because the optimum solubility varies from about 17 for T_1 to about 10 for T_3 . An optimum solubility of 10 may not generate the ultra-low interfacial tension needed to mobilize residual oil saturation, while a value of 17 would be sufficient. **Fig 3.4** illustrates the values in Fig 3.3 denoted by the squares for a temperature scan at fixed P_1 .



Fig 3. 1 Illustration of characteristic length within a three-phase microemulsion under various hydrophobicity conditions: a. hydrophilic, b. hydrophilic-lipophilic, c. lipophilic. Blue is water, gray is oil, and the black interface is a surfactant layer. The "repeatable" areas are shown by the rectangles and their corresponding equivalent volumes as hypothetical spheres shown in d, e, and f. Circles in d and f are illustrated to have same size, however in this chapter we demonstrate that those sizes are different in the three-phase transition.



Fig 3. 2 Illustration of characteristic length at different optimums within a three-phase region. The characteristic length should vary with changes in temperature and pressure.



Fig 3. 3 Illustration of pressure scans at three fixed temperatures.



Fig 3. 4 Illustration of a temperature scan at fixed pressure P_1 .

3.2.3 Characteristic Length and Gibbs Phase Rule

The functional form to describe the variation in the characteristic length depends on the degrees of freedom as determined by the Gibbs phase rule. For a three-component system (brine, oil, surfactant) with three phases, the Gibbs phase rule states there are two degrees of freedom to determine the intensive state of the system. EACN and salinity can also change, but if they both vary the number of components must be increased by two and degrees of freedom are therefore four. In terms of these variables, we can then write the functional form as $\xi_D^{3\phi} = f(S, EACN, T, P)$. The degrees of freedom could be increased further by adding other variables, such as the alcohol chain length and number of EO groups in the surfactant and so forth.

Ghosh and Johns (2016a) showed that the inverse of the characteristic length varies linearly with formulation variables. Other authors proposed similar correlations for optimum solubilization ratio (or characteristic length) that defines the size of three-phase zone (Barakat et al., 1983; Acosta et al., 2008). Thus, we propose a general form for characteristic length in a three-phase region as

$$d\left(\frac{3I}{\xi_D^{3\phi}}\right) = \sum_i \frac{\partial}{\partial v_i} \left(\frac{3I}{\xi_D^{3\phi}}\right)|_{j\neq i} dv_i ,$$

where v_i is a thermodynamic formulation variable where the number of variables are constrained by the Gibbs phase rule. The group $3I / \xi_D^{3\phi}$ includes the I-ratio to incorporate

any uncertainty in the value of the I-ratio. This is similar to the grouping of parameters in cubic equations of state for vapor-liquid equilibrium (Sandler, 2006).

In this chapter we use $v_i = f(S, EACN, T, P)$. Thus, the functional form for the characteristic length becomes,

$$d\left(\frac{3I}{\xi_{D}^{3\phi}}\right) = \frac{\partial}{\partial \ln S} \left(\frac{3I}{\xi_{D}^{3\phi}}\right)_{T, EACN, P} d\ln S + \frac{\partial}{\partial EACN} \left(\frac{3I}{\xi_{D}^{3\phi}}\right)_{T, S, P} dEACN + \frac{\partial}{\partial T} \left(\frac{3I}{\xi_{D}^{3\phi}}\right)_{S, EACN, P} dT + \frac{\partial}{\partial P} \left(\frac{3I}{\xi_{D}^{3\phi}}\right)_{S, EACN, T} dP$$

For constant partial derivatives, we arrive at the following expression:

$$d\left(\frac{3I}{\xi_D^{3\phi}}\right) = \lambda_s d\ln S + \lambda_{EACN} dEACN + \lambda_T dT + \lambda_P dP,$$

where the λ_i values are equal to the partial derivatives. The assumption of constant partial derivatives is reasonable for small changes in the variables as evidenced by experimental data. Integration then gives the desired result:

$$\frac{3I}{\xi_{D}^{3\phi}} = \frac{3I}{\xi_{Dref}^{3\phi}} + \lambda_{T} \left(T - T_{ref}\right) + \lambda_{P} \left(P - P_{ref}\right) + \lambda_{s} \ln \frac{S}{S_{ref}} + \lambda_{EACN} \left(EACN - EACN_{ref}\right) .$$
(4)

We define the reference state to be any one optimum state. For example, if only a temperature scan is considered for a given system, the reference characteristic length is the optimum temperature of that scan. All other terms on the right-hand side of Eq. (4) would then be zero because those parameters would be fixed. That is, $3I / \xi_D^{3\phi} = 3I / \xi_{Dref}^{3\phi} + \lambda_T (T - T_{ref}).$
There are physical limits for characteristic length (de Gennes and Taupin, 1982). We cannot physically have a negative characteristic length so that $3I/\xi_D^{3\phi} > 0$. In the Khorsandi and Johns (2016) methodology, however, negative three-phase zones are used to model the two-phase lobes when the three-phase region is no longer present in positive composition space. For this mathematical representation, the characteristic length could be negative, although in this chapter we only use a positive characteristic length.

3.2.4 Flash calculation algorithm including variable characteristic length

The model for variable characteristic length is incorporated into our current HLD-NAC model developed by Khorsandi and Johns (2016) that includes modeling of the twophase lobes. Fig 3.5 gives the flowchart for the updated flash calculation algorithm. The primary inputs for the flash calculation are temperature, pressure, and the overall composition, while the outputs are saturations and the microemulsion phase composition. EACN and salinity are input to define the oil and brine pseudo components, similar to how critical temperature, critical pressure, and acentric factor are used to define components for vapor-liquid equilibrium calculations with cubic equations-of-state. The excess phases are approximated as pure oil or water pseudo component even though they are not quite pure as shown by the definition of HLD. Like vapor-liquid flash calculations with cubic EoS, there are also additional EoS parameters: coefficients for the HLD equation, coefficients for the $\xi_D^{3\phi}$ correlation, the *I* - ratio and the C_1, C_2 coefficients for the critical tie-line parameterization. These coefficients are determined by tuning to experimental data. First estimates of these coefficients are typically made using graphical methods and then finetuned with simultaneous regression (see Khorsandi and Johns). In the procedure that follows, we assume all coefficients are known and the surfactant composition is greater than the critical micelle concentration (CMC).

The first step in the flash calculation procedure is to calculate the value of HLD based on Eq. (5), where we allow for variations in salinity, temperature, pressure and oil type (EACN). The reference state in Eq. (5) is typically chosen based on any one measured optimum state, where the value of HLD at the reference state is arbitrarily set to zero ($\mathcal{H}_{ref} = 0$) as described earlier. Other variables can be added to the functional form as needed (Salager et al., 2000).

$$\mathcal{H} = \mathcal{H}_{ref} + \ln \frac{S}{S_{ref}} + \alpha \left(T - T_{ref} \right) + \beta \left(P - P_{ref} \right) + K \left(EACN - EACN_{ref} \right)$$
(5)

Next, we check whether the three-phase region exists in positive composition space. A three-phase region exists in the ternary diagram when $|\mathcal{H}^{l}| \leq 2/\xi_{D}^{3\phi}$, where Eq. (4) is used to calculate the dimensionless characteristic length of the microemulsion phase in the three-phase region. Unlike in Khorsandi and Johns (2016), the value of $\mathcal{H}^{l} = 2/\xi_{D}^{3\phi}$ changes with salinity, temperature, pressure, and EACN. That is, the negative and positive values of HLD are not equal because the characteristic length now varies and is different at these limits. If the three-phase region does not exist in positive composition space, we consider a two-phase flash calculation for either type II- or type II+ as is done in Khorsandi and Johns (2016). In their procedure, the three-phase region still exists, but only in negative composition space. That is, the three-phase microemulsion phase composition moves outside the ternary diagram but is still calculated using the same equations. This methodology allows for consistency between the two-phase and the three-phase regions, by accounting for the value of the characteristic length at the boundary of the hypothetical three-phase region and how far the three-phase region is from entering the ternary diagram.

The three-phase solubilization ratios of any "positive" or "negative" three-phase region are calculated using the dimensionless HLD-NAC model (Ghosh and Johns, 2016b). These ratios determine the boundary tie lines of the tie triangle, where

$$\sigma_{w}^{3\phi} = \frac{2}{3I(\mathcal{H} + \mathcal{H}^{l})} , \qquad (6)$$

$$\sigma_o^{3\phi} = -\frac{2}{3I\left(\mathcal{H} - \mathcal{H}^t\right)} \,. \tag{7}$$

The tie lines at the boundary of the three-phase region (tie triangle) are at the limits of the type II- and II+ regions. Because of the assumption of pure excess phases, each tie line can be characterized using the intercept parameter proposed by Khorsandi and Johns (2016), where the intercept parameters are the surfactant composition at the intersections of the tie lines with the zero oil and zero water axis of the ternary diagram. These parameters are calculated using the following equations:

$$b_{-}^{3\phi} = 1/(1 + \sigma_{w}^{3\phi}) , \qquad (8)$$

$$b_{+}^{3\phi} = 1/(1+\sigma_{o}^{3\phi}) .$$
(9)

For three-phase regions inside the ternary diagram, we test whether the overall composition lies within that three-phase region. This is a simple test based on the tie-line intercepts and the overall composition. We draw a line from the specified overall composition to both the water and oil apex and then extend that line to intersect the zero oil or zero water axis of the ternary diagram. The surfactant composition at the intersection points is given by,

$$b_{z-} = C_s / (C_s + C_w) , \qquad (10)$$

$$b_{z+} = C_s / (C_s + C_o) . (11)$$

The overall composition could also be in either the type II-, II+, or type IV regions. Thus, we must also determine the limiting tie line at the critical points, which lie on the water and oil apex of the ternary diagram. As shown by Khorsandi and Johns (2016), the dimensionless critical characteristic length is calculated using the following correlation:

$$\frac{3I}{\xi_{D-}^{c}} = C_1 \left(e^{C_2(\mathcal{H}^{l} - \mathcal{H})} - 1 \right) + \frac{3I}{\xi_D^{3\phi}}$$
(12)

$$\frac{3I}{\xi_{D+}^{c}} = C_1 \left(e^{C_2(\mathcal{H}^{l} + \mathcal{H})} - 1 \right) + \frac{3I}{\xi_D^{3\phi}} , \qquad (13)$$

where the critical characteristic length is a function of the varying three-phase dimensionless characteristic length at the boundary of the two-phase lobe and HLD (the degrees of freedom for a critical point in a ternary diagram are two). Equations (12) and (13) give the proper limits where the characteristic length is equal to the critical characteristic length when the three-phase region just disappears from positive composition space. The values of C_1 and C_2 are determined by tuning. These values can be different in the type II- and II+ regions.

Once the critical characteristic length is determined, we calculate the critical solubilization ratio with the criticality conditions for the corresponding two-phase lobe as $1/\sigma_w^c = 6I/\xi_{D-}^c$ and $1/\sigma_o^c = 6I/\xi_{D+}^c$. More details on the criticality condition derivation can be found in Khorsandi and Johns (2016). From the critical solubilization ratios we obtain the surfactant composition at the intersections of the limiting critical tie lines with the ternary axes as,

$$b_{-}^{c} = 1/(1 + \sigma_{w}^{c}) , \qquad (14)$$

$$b_{+}^{c} = 1/(1+\sigma_{o}^{c}) .$$
 (15)

We use linear interpolation of the characteristic length based on these intercepts to calculate the characteristic length for tie lines within the two-phase lobes. The slope is

determined from the two limiting tie lines, one at the critical tie line and the other at the boundary tie line of the three-phase region. That is,

$$A_{-} = \frac{3I / \xi_{D-}^{c} - 3I / \xi_{D}^{3\phi}}{b_{-}^{c} - b_{-}^{3\phi}} .$$
 (16)

$$A_{+} = \frac{3I / \xi_{D+}^{c} - 3I / \xi_{D}^{3\phi}}{b_{+}^{c} - b_{+}^{3\phi}}$$
(17)

where type II- and type II+ have different values of the slope $A_{-/+}$. Then, the characteristic length for a tie-line at a specified overall composition in the two-phase region is determined by

$$\frac{3I}{\xi_D^{2\phi-}} = \frac{3I}{\xi_{D-}^c} - A_- \left(b_-^c - b_{z-} \right)$$
(18)

$$\frac{3I}{\xi_D^{2\phi_+}} = \frac{3I}{\xi_{D_+}^c} - A_+ \left(b_+^c - b_{z_+} \right) \,. \tag{19}$$

One of the keys to the flash calculations is to identify the Winsor type at a specified overall composition using the series of tie-line intercept parameters defined above. The overall composition lies within the type III region when $b_{z-} < b_{-}^{3\phi}$ and $b_{z+} < b_{+}^{3\phi}$. Type II-calculations are made when the overall composition lies between the three-phase tie line and type II- critical tie line, i.e. $b_{-}^{c} > b_{-}^{3\phi}$. The algorithm ends if after type II-calculations $S_m < 1$, i.e. $C_3 < C_3^m$; if not, type II+ calculations are initiated. Type II+ is expected if an overall composition tie line lies between the three-phase tie line and type

II+ critical tie line, i.e. $b_{+}^{c} > b_{z+} > b_{+}^{3\phi}$. The flash calculation ends if after type II+ calculations $S_m < 1$, i.e. $C_3 < C_3^m$; if not, then the phase behavior is type IV and the overall composition lies in the single-phase region.

Example flash calculation with new algorithm

Table 3.1 gives three example calculations for the proposed flash algorithm in Fig 3.5 for various overall compositions and Winsor types. Flash calculation route shows the path taken during the flash calculation for model inputs presented in the Table 3.1. The calculations are conducted using model parameters shown in **Table 3.2**, where only salinity is changing, and other formulation variables are fixed.

Model inputs	Flash	Flash output
	calculation	
	route	
$C_w = 0.48, C_o = 0.5, C_s = 0.02, S = 1.05\%$	wt a-b-c-d-i	$C_s^m = 0.044, C_w^m = 0.404, C_s^m = 0.552, S_m = 0.451$
	(type III)	3 W U M
$C_w = 0.94, C_o = 0.05, C_s = 0.01, S = 1.05$	% wt a-b-c-g-h-i	$C_{s}^{m} = 0.060, C_{w}^{m} = 0.643, C_{o}^{m} = 0.297, S_{w} = 0.168$
	(type II+)	5 w 0 m
$C_w = 0.40, C_o = 0.53, C_s = 0.07, S = 1.05$	% wt a-b-c-e-f-g-h-i	$C_s^m = 0.07, C_w^m = 0.40, C_a^m = 0.53, S_m = 1$
	(type IV)	5 w 0 m

Table 3. 1 Sample calculations for S=1.05 % wt with only salinity varying.

Table 3. 2 Model parameters for equation-of-state sample calculations with only salinity varying. The parameters C_1 and C_2 are assumed to be the same for type II- and II+.

${\cal H}$ parameters	$\mathcal{H} = \ln(S/1)$
$\xi_D^{3\phi}$ parameters	$3I / \xi_D^{3\phi} = 0.083 + 0.240 \ln(S/1)$
Ι	0.2
C_1	0.3
	1



Fig 3. 5 Equation-of-state algorithm to include characteristic length variation in the three-phase region.

3.3 Results and discussion

We use a variety of experimental data in this section to demonstrate the importance of a variable characteristic length model on phase behavior tuning and prediction. Moreover, we show that the three-phase variable characteristic length also impacts the size and occurrence of the two-phase lobes.

Dead oil pressure and temperature scans from Austad and Strand (1996)

Experimental evidence shows that the three-phase characteristic length varies as a function of formulation variables, including temperature, pressure, salinity, and oil type (EACN). We consider first a set of experimental data from Austad and Strand (1996) with only temperature and pressure varying.

Fig 3.6 shows the measured dimensionless characteristic length as a function of pressure for a wide range of fixed temperatures. The trends with pressure are nearly linear and demonstrate a large change in the dimensionless characteristic length. Also shown are the values for an average constant characteristic length, which would give a significant error.

The same data in Fig. 6 is plotted in **Fig 3.7**, but as a function of both temperature and pressure. The figure shows an almost perfectly planar surface of characteristic length as a function of temperature and pressure. This confirms the use of constant partial derivatives for the coefficients in Eq. (4), at least for this example.



Fig 3. 6 Phase behavior data for pressure scans of dead oil. Comparison of variable and constant characteristic length. Dead oil data from Austad and Strand (1996). The proposed formulation here is a best fit to Eq. (4) with only pressure and temperature varying.

Fig 3.8 shows the oil and water solubility ratios with varying pressure at a fixed temperature of 70°C using the updated flash calculation algorithm and the correlation from Eq. (4) in Fig. 7. **Table 3.3** shows the model parameters used for Fig. 8. The results show excellent agreement to the experimental data compared to the Khorsandi and Johns (2016) approach. That is, the new algorithm allows for matching the asymmetric phase behavior around the optimum for changes in solubilities and the microemulsion composition (invariant locus) with pressure. Other temperatures give similarly good agreement.

Live oil pressure and temperature scans from Austad and Strand (1996)

We now consider the live oil data from Austad and Strand (1996) where temperature and pressure vary at fixed EACN and salinity. Methane mole fraction in the live oil is reported to be constant at 35%. Fig 3.9 shows that the characteristic length varies significantly as a function of pressure and temperature instead of being constant. The correlation given by Eq. (4) approximates the trend in characteristic length well, although the fit is not as good for the lower pressure data and also compared to the dead oil data. This increased error in live oil data is likely a result of the compressibility corrections used for the excess phase volumes as a function of temperature and pressure. The adjustments for the live oil data were not as accurate as those for the dead oil in that the compressibility was much larger for the live oil (excess oil phase) and there was no measurement below 150 bars.



Fig 3. 7 Three-phase characteristic length as a function of both temperature and pressure, represented as a planar surface using Eq. (4), where the constant in the equation includes all reference values. The planar surface is shown in the right figure. Dead oil data from Austad and Strand (1996).



Fig 3. 8 a. Improved fit of the solubilities in the three-phase region using the variable characteristic length. b. Microemulsion phase composition invariant locus. The asymmetric phase behavior around the optimum is now captured. Dead oil data from Austad and Strand (1996) are shown by the symbols for 70°C. The solid lines are the updated model with a variable three-phase characteristic length, while the dashed curves are the predicted values after tuning with the Khorsandi and Johns (2016) EoS.

Inputs/parameters	Proposed model	Khorsandi and Johns (2016)
Р	$0 \rightarrow 300$	$0 \rightarrow 300$
\mathcal{H}	$\mathcal{H} = -7 \times 10^{-4} \left(P - 150 \right)$	$\mathcal{H} = -7 \times 10^{-4} \left(P - 150 \right)$
$\xi_D^{3\phi}$	$3I / \xi_D^{3\phi} = 0.0855 - 9.23 \times 10^{-5} (P - 150)$	$3I / \xi_D^{3\phi} = 0.0870$
Ι	0.27	0.27
	0.3	0.3
C ₂	1	1

Table 3. 3 Model inputs for proposed model and Khorsandi and Johns (2016).



a.

Fig 3. 9 Phase behavior in the three-phase region for temperature scans of live oil at fixed EACN and salinity. a. Comparison of variable and constant characteristic length. b. Eq. (4) fit of pressure and temperature data. Data from Austad and Strand (1996).

Salinity and EACN scans from Chou and Bae (1988)

In Fig 3.10, the salinity and EACN are varied within the reported three-phase region at fixed temperature and pressure (see Chou and Bae, 1988). As shown, the three-phase characteristic length generally increases with salinity and EACN. The change in characteristic length is more significant for a change in EACN than for the logarithm of salinity. The fit to the correlation in Eq. 4 is very good as shown.

The trend in Fig. 10 is not monotonic with salinity likely because of the uncertainty in the calculation of the characteristic length. A simple calculation shows that the relative error in $3I/\xi_D^{3\phi}$ is around 5 to 10%, or an absolute maximum error of about 0.01 for the data in Fig. 10. Thus, we should not expect the trends to be clearly identified by the experimental data. Still, when all data is used in the fitting process with Eq. (4), the change in $3I/\xi_D^{3\phi}$ with lnS is positive.



Fig 3. 10 a. Three-phase characteristic length as a function of the logarithm of salinity and EACN at fixed temperature and pressure. b. Eq. (4) fit of log salinity and EACN data. The data is from Chou and Bae (1988).

Salinity scans from Roshanfekr and Johns (2010)

We used data for varying salinity and EACN at fixed pressure and temperature (Roshanfekr, 2010, Roshanfekr and Johns, 2011). Their data shows a general trend of increasing characteristic length with EACN and salinity, although for the smaller EACN case the characteristic length decreased somewhat with salinity (see **Fig 3.11**). This decrease in $3I / \xi_D^{3\phi}$ within the three-phase region is within the range of uncertainty in its calculation as described earlier. Furthermore, the system of pure n-alkanes used by Roshanfekr did not equilibrate quickly, which may also cause additional uncertainty.

As shown in Fig. 11, the variations in the characteristic length are almost entirely due to a change in EACN. The fit to the data is good by Eq. (4) and would be substantially better to use than assuming a constant characteristic length. **Table 3.4** summarizes the best fit parameters for the variable characteristic length that are used for this data set, and for the prior ones. The constant in the table accounts for the reference values.



Fig 3. 11 a. Three-phase characteristic length as a function of logarithm of salinity and EACN at fixed temperature and atmospheric pressure. b. Eq. (4) fit of log salinity and EACN data. Data from Roshanfekr (2010). The EACN variation is the result of using different pure n-alkanes (octane, decane, dodecane).

Figure	$3I/\xi_D^{3\phi}$	Data reference
Fig 3.6	$3I / \xi_D^{3\phi} = 4.4 \times 10^{-2} - 9.2 \times 10^{-5} P + 8.0 \times 10^{-4} T$	Austad and Strand (1996)
Fig 3.9	$3I / \xi_D^{3\phi} = 4.4 \times 10^{-2} - 6.0 \times 10^{-5} P + 5.9 \times 10^{-4} T$	Austad and Strand (1996)
Fig 3.10	$3I / \xi_D^{3\phi} = -2.6 \times 10^{-1} + 1.3 \times 10^{-1} \ln S + 8.3 \times 10^{-3} EACN$	Chou and Bae (1988)
Fig 3.11	$3I / \xi_D^{3\phi} = -2.7 \times 10^{-2} + 2.3 \times 10^{-2} \ln S + 1.0 \times 10^{-2} EACN$	Roshanfekr (2010)

Table 3. 4 Parameters used to model experimental data with Eq. (4).

Effect of three-phase variable characteristic length on two-phase lobes

There is limited experimental data on the impact of variable characteristic length on the two-phase lobes. Thus, in this section we illustrate that use of a variable characteristic length likely significant impacts the two-phase lobes in addition to the threephase region.

Fig 3.12 shows phase behavior changes at fixed overall composition using both the updated EOS with variable characteristic length, and the prior version from Khorsandi and Johns (2016) with a constant characteristic length. Fig 3.12 a,b using the Khorsandi and Johns algorithm shows a symmetric two-phase lobe around optimum with changes in HLD, while Fig 3.12 c,d shows that the use of a variable characteristic length gives significant asymmetry around the optimum condition. Moreover, we observe that the sizes of the two-phase lobes are affected by the use of a variable characteristic length. The type II+ lobe is larger, while the type II- lobe is smaller compared to using a constant characteristic length at the same values of HLD.

Table 3.2 gives the model parameters used in Fig 3.12 for both the proposed and Khorsandi and Johns (2016) models. All model inputs were the same for both models, except the characteristic length is constant ($\lambda_s = 0$) for the latter. Only salinity is varying in this example.



Fig 3. 12 Effect of variable characteristic length on two-phase lobes, $S^* = 1.0$ % wt.: a. constant length with S=1.05% wt. (HLD=0.1); b. constant characteristic length with S=0.905% wt. (HLD=-0.1); c. variable characteristic length with S=1.05% wt. (HLD=0.1); d. variable characteristic length with S=0.905 % wt. (HLD=-0.1).

3.4 Chapter 3 conclusions

This chapter examined the change in characteristic length in the three-phase region with formulation variables such as temperature, pressure, salinity and EACN. The variable characteristic length was then included in the Khorsandi and Johns (2016) EoS. The following key conclusions are made:

- Characteristic length varies inversely with most formulation variables as evidenced by experimental data. Salinity impacts characteristic length much less, however, than the other formulation variables.
- 2. The use of a variable characteristic length allows for asymmetric phase behavior modeling on either side of the optimum. This improvement can be very important, especially for three-phase regions that exist over a large change in HLD. Significantly improved fits to experimental data were demonstrated.
- 3. The asymmetry caused by a variable characteristic length affects the size of two-phase lobes as well. This occurs because the boundary of the threephase region is also the boundary of the two-phase lobes.

3.5 Chapter 3 nomenclature

Symbols	Description
C_i	Overall volume fraction of pseudocomponent $i = w, o, s$, water, oil, surfactant
C_i^j	Volume fraction of pseudocomponent in phase $j = w, o, m$
${\cal H}$	Hydrophilic-lipophilic deviation (HLD)
ν	Formulation variable, such as temperature, pressure, and composition
v^*	Optimum condition for formulation variables
S	Salinity (wt%)
Κ	Partial derivative of HLD with oil type (EACN)
EACN	Oil pseudocomponent, equivalent alkane carbon number
α	Partial derivative of HLD with temperature (${}^{o}C^{-1}$)
Т	Temperature (°C)
β	Partial derivative of HLD with pressure (bar ⁻¹)
Р	Pressure (bar)
ref	Reference state
$\xi_D^{3\phi}$	Dimensionless three-phase characteristic length
$\xi_D^{2\phi-/2\phi+}$	Dimensionless two-phase characteristic length
$\xi^c_{D\!-\!/D\!+}$	Dimensionless critical characteristic length for two-phase lobes
$A_{-/+}$	Slope for two-phase characteristic length calculations
$\lambda_{_{\mathcal{V}}}$	Partial derivative of three-phase characteristic length with formulation variable
S_{j}	Saturation of phase <i>j</i>
$\sigma^{\scriptscriptstyle 3\phi}_{\scriptscriptstyle o/w}$	Solubilization ratio of oil or water (ratio of oil or water volume per surfactant volume
Ι	Interfacial volume ratio parameter
\mathcal{H}^{l}	HLD limit of the existing positive three-phase region
$b^c_{\scriptscriptstyle -\!/\!+}$	Critical point intercept of type II-/II+ two-phase lobe
$b_{_{7-/7+}}$	Overall composition tie-line intercept
$b^{3\phi}_{_{-/+}}$	Tie-triangle intercept

Chapter 4 Improved Equation-of-State Modeling for Surfactant-Oil-Water Systems

Chapter Summary

In this chapter, we significantly extend recently developed physics-based equationof-state (EoS) models, which use the hydrophilic-lipophilic deviation (HLD) and netaverage curvature (NAC) equations. We extend the microemulsion flash calculation algorithm presented in Chapter 3. First, we rigorously define HLD in terms of the surfactant partitioning between oil and brine phases. Second, we rewrite the EoS in terms of oil and water component partitioning between oleic/brine and microemulsion phases (Kvalues). Interpolation and extrapolation of these K-values using a power-law expression is made to model more accurately the two-phase regions and the limiting tie line at the critical point. Third, the use of K-values shows for the first time that the physical size and shape of the two-phase lobes are restricted to lie within a region defined by the three-phase boundaries. Lastly, we relax the assumption that the excess phases must be pure by considering two critical micelle concentrations (CMC), one on the surfactant-oil and the other on surfactant-brine axis of the ternary diagram. The values of these CMCs depend on the K-values and also are made consistent with the Gibbs phase rule, i.e. are functions of two state variables. For the first time, the angle between the rays extended from the microemulsion-oil and microemulsion-brine boundaries of the three-phase region must always be at 60 degrees when the excess phases are pure (contain only oil or water). This result is also true when the excess phases contain surfactant. Thus, the new EoS could be important for the accurate design and modeling of microemulsion phase behavior for oil-water-surfactant systems.

4.1 Introduction

A flash calculation determines equilibrated phase compositions and phase amounts at a specified temperature, pressure, and overall composition (Li et al., 2012). The multiphase system is in equilibrium when chemical potentials of every component are equal across all phases. Equilibrium can be expressed as equal fugacities or given equilibrium ratios (K-values) (Sandler, 2006). A flash calculation with specified equilibrium K-values for the multicomponent system is a non-trivial task and has been addressed in the literature extensively. Rachford-Rice (1952) proposed the method to solve for two-phase amounts, and that method requires an accurate initial guess. The window for the correct solution was proposed to obtain a more accurate initial estimate and to avoid potential poles in the solution (Whitson and Michelsen, 1989). Li et al. (2012) made a significant advancement for robust two-phase negative flash calculation that solves for both positive and negative compositional space calculations. A more sophisticated flash calculation procedure is required when more than two-phases exist in equilibrium (Nelson, 1987, Bunz et al., 1991, Okuno et al., 2010). In this chapter we further extend the microemulsion flash calculation algorithm proposed in Chapter 3. We combine HLD-NAC

based flash calculation algorithm and equilibrium K-values approach to improve phase behavior modelling.

Khorsandi and Johns (2016) proposed an approach to model continuous two-phase zones by using the critical characteristic length equation and linear interpolation between a critical point and the tie triangle. However, the two-phase lobes are under-constrained and the current model may result in unphysical overlap of two-phase lobes. In this chapter, we consider the limiting case of constant equilibrium K-values to constrain the sizes of two-phase lobes. Moreover, we use the K-value information to further model continuous two-phase lobes instead of using characteristic length interpolation within two-phase lobes proposed in previous HLD-NAC based models. Characteristic length within the two-phase equilibrium is somewhat difficult to interpret because one phase becomes continuous and the other is dispersed. Therefore, K-value information and trends between the three-phase tie triangle and critical point can provide valuable insights for flash calculation.

The main objective of this research is to consider limiting cases that will define physical constraints for microemulsion flash calculations and to update a flash calculation algorithm for a water/oil/surfactant system. The Chapter 1s organized as follows. First, we discuss the Gibbs phase rule for HLD. Second, oil-brine flash calculation and surfactant partitioning model are presented. Third, we introduce constant K-value constraints for twophase zones and present a full flash calculation algorithm. Fifth, we match and predict experimental microemulsion phase behavior data using the proposed updated equation of state model. Last, we present the conclusions of this chapter.

4.2 Methodology

The methodology section defines the hydrophilic-lipophilic deviation in terms of Gibbs phase rule. Further, the surfactant partitioning model and coordinate transform procedures are presented. Lastly, the flash calculation algorithm and phase diagram examples are constructed.

4.2.1 HLD definition based on Gibbs phase rule

HLD (or \mathcal{H} as will be used in mathematical equations) was introduced originally by Salager et al. (2000), using equality of chemical potentials of the surfactant component in the excess phases. The surfactant hydrophilic-lipophilic deviation (HLD) is generally defined as zero when the amount of surfactant in the brine and oil phases is perfectly balanced by volumetric concentration. The HLD correlation is based on relationships in the three-phase region (Salager et al. 1979).

A general and rigorous way to define HLD is based on it being a state function. Thus, in differential form as a function of independent variables (Salager et al. 2013),

$$d\mathcal{H} = \sum_{i} \frac{\partial \mathcal{H}}{\partial v_{i}} \bigg|_{v_{j \neq i}} dv_{i}$$
(1)

where \mathcal{H} is HLD and v_i is a state variable (formulation variable). The Gibbs phase rule governs the number of parameters needed for the intensive state of the system to be

specified. HLD is normally applied only to the three-phase region, although we use it to define the boundaries of the two-phase lobes in the EoS.

The HLD equation is solved here assuming the partial derivatives are constant, which is a reasonable assumption based on experimental results. The equation is often written incorrectly. HLD is defined based on the surfactant partitioning coefficient between oil and brine. The literature on this is confusing, so we first define HLD more carefully.

For common state function variables and use of a reference point (set of state variables where data is measured), integration of the HLD definition (Eq. 1) gives for anionic surfactants,

$$\mathcal{H} = \mathcal{H}_{ref} + \ln\left(\frac{S}{S_{ref}}\right) - K\left(EACN - EACN_{ref}\right) - \alpha\left(T - T_{ref}\right) - \beta\left(P - P_{ref}\right)$$
(2)

where, *S* is the salinity of the aqueous phase (representing the water pseudocomponent), *EACN* is the equivalent alkane carbon number (representing the oil pseudocomponent), P is the pressure and T is the temperature. The above result assumes that partial coefficient for salinity is equal to one. However, it does not have to be. Appendix D discusses using a coefficient other than 1.0 and applicability of HLD-NAC based models within three-phase zone. The Appendix D discusses how uncertainty of partial coefficients are taken care of in the I-ratio for HLD-NAC models.

The choice of the number of parameters (state variables) to use depends on the Gibbs phase rule (number of components and number of phases). Equation (2) assumes four state variables, but how many are possible to use depends on the Gibbs phase rule. In that case it is for three-phase, five-component systems, where the degrees of freedom are 4. The components are oil 1, oil 2, brine 1, brine 2, and surfactant.

There is no reason to introduce HLD at all. For example, one could just use the K-value for surfactant partitioning in the oil-brine phases. Salager defined HLD in this way, but again there has been some confusion here. A multitude of experiments shows that K_s^{ow} changes linearly with most state variables in both the two and three-phase regions (Salager et al., 2000, Torrealba and Johns, 2018). If we assume this, we can define and essentially eliminate HLD completely in favor of the K-value:

$$d\mathcal{H} = d\ln K_3^{ow} \quad . \tag{3}$$

where, $K_3^{ow} = C'_{3o}/C'_{3w}$, $K_i^{\alpha\beta}$ is an equilibrium constant of pseudocomponent *i* between phases α and β , i = 1 (water), 2 (oil), 3 (surfactant), C'_{ij} is the volume fraction of pseudocomponent *i* in phase: j = w (aqueous), *o* (oil), *m* (microemulsion). The surfactant partitioning coefficient between oil and brine is used by Salagar et al. (2000) to define HLD. Salager's group also found from numerous experiments the relationship between partitioning coefficient and surfactant ethoxy groups (*EON*) for nonionic surfactants (Marquez et al., 1995, Marquez et al., 2003, Graciaa et al., 2006), which is not discussed here.

What are the assumptions involved in deriving the above? This is the exact definition of HLD we use here, which means that HLD is just a proxy for the K-value in Eq. (3). Thus, combining (1) and (2) gives,

$$\mathcal{H} = \mathcal{H}_{ref} + \ln\left(\frac{K_{S}^{ow}}{K_{Sref}^{ow}}\right) = \mathcal{H}_{ref} + \ln\left(\frac{S}{S_{ref}}\right) - K\left(EACN - EACN_{ref}\right) - \alpha\left(T - T_{ref}\right) - \beta\left(P - P_{ref}\right) \quad (4).$$

We can choose the reference state, and then define the arbitrary value of HLD at this reference state. This is because state function changes are always determined with respect to a reference point (from thermodynamics and mathematics). A good choice is at an observed optimum (any optimum will do), where we also set \mathcal{H}_{ref} to be zero. Thus, with * indicating an optimum we have,

$$\mathcal{H} = \ln\left(\frac{K_{S}^{ow}}{K_{Sref}^{ow^{*}}}\right) = \ln\left(\frac{S}{S_{ref}^{*}}\right) - K\left(EACN - EACN_{ref}^{*}\right) - \alpha\left(T - T_{ref}^{*}\right) - \beta\left(P - P_{ref}^{*}\right)$$
(5)

The K-value does not need to be 1.0 at optimum (equal partitioning of surfactant in oil and brine phases, equal solubility, or equal CMC in brine and oil). Ideally, this K-value should be measured when interfacial tensions are equal (the defined optimum). Good

surfactants for EOR will generally achieve equal partitioning, so we will assume that here. The literature nearly always assumes the K-value is 1.0 however, so that $\ln K_{Sref}^{ow} = 0$.

4.2.2 Surfactant partitioning model

Surfactant may partition into brine or oleic phases. From a chemical enhanced oil perspective, surfactant that partitions into oleic and/or brine phase becomes inactive and does not contribute to the interfacial phenomena. Thus, it is important to account for surfactant partitioning in the phase behavior modelling.

We use HLD developed by Salager's group for the surfactant K-value partitioning between aqueous and oleic phases (see 4.2.1 section). However, one K-value itself does not provide complete information about surfactant partitioning into both phases, so we need additional information. We need one more intrinsic thermodynamic property to characterize surfactant partitioning into oleic and aqueous phases. We propose to use critical micelle concentration of surfactant in brine phase, C_{3w} , as an additional intrinsic property.

When a small amount of surfactant is added to the aqueous solution the surfactant monomers disperse in the phase without aggregation into micelles (Rosen, 2004). Adding more surfactant to the system saturates the phase. Beyond a certain concentration the surfactants aggregate into micelles to form a microemulsion phase. This reduces overall free energy of the system. The concentration at which micelles start forming is referred to as the critical micelle concentration (CMC) (Bourrel and Schecter, 2010). It is argued that microemulsions are formed when surfactant concentration is above the CMC (Kumar and Mittal, 1999). Critical micelle concentration of surfactants in the aqueous phase have been studied extensively. Corrin and Harkins (1947) demonstrated a linear relationship between CMC and sodium chloride concentration on a log-log scale for anionic and cationic surfactants, i.e. $\ln C_{3w} \sim \ln C_{salt}$. Klevens (1953) have shown a linear relationship between surfactant hydrophobic tail length and the logarithm of CMC, i.e $\ln C_{3w} \sim L_{surf}$. Rodriguez and Offen (1976) observed near-linear dependence with pressure, i.e $\ln C_{3w} \sim P$. As was mentioned before, variations of salinity, surfactant structure, and pressure can be expressed as variations in HLD.

From Fig 4.1 the logarithm of the surfactant partitioning K-value into the aqueous phase (CMC) has a linear dependency on EACN. The original data was in weight fraction. Thus, the data are converted to volume fraction using alkane densities from Diaz Pena and Tardajos, 1978. We assume density of water and solution surfactant to be equal. As was mentioned previously, the logarithm of the aqueous CMC showed a linear relationship with pressure, surfactant structure, and logarithm of salinity. Those formulation variables are related to HLD, as was shown before. In this chapter, we propose a relationship for surfactant partitioning into aqueous phase as:



Fig 4.1 Linear trend of ln(CMC) and EACN. Squares are experimental data. Red squares are used for linear regression, blue triangle for prediction. Data from Kilpatrick et al. (1986).



Fig 4.2 Linear trend of $ln(K_3^{wo})$ and EACN. Squares are experimental data. Red squares are used for linear regression, blue triangle for prediction. Data from Kilpatrick et al. (1986).

$$C'_{3w} = C'^{ref}_{3w} \exp(-a\mathcal{H}),$$

where, C_{3w}^{ref} is a reference surfactant partitioning at HLD of zero, and *a* is a slope of log of aqueous CMC and HLD. There is partitioning of surfactant into the oleic phase, and the experiments by Salager's group show that HLD is related to surfactant partitioning coefficient for brine and oleic phases (Marquez et al., 1995, Marquez et al., 2003, Graciaa et al., 2006). Thus, we use the HLD definition and proposed a model for CMC to find surfactant partitioning into oleic phase as:

$$C'_{3o} = C'_{3w} K_3^{ow} = C'_{3w}^{ref} \exp((1-a)\mathcal{H})$$
.

To satisfy the HLD definition, the value of a should be in the range 0 < a < 1. For symmetry, one would need to use a = 0.5. The above equation takes Gibbs phase rule into account via use of HLD. For example, if T and P are changing the HLD value will change accordingly. Thus, surfactant partitioning will be a function of T and P through HLD.

After determining surfactant partitioning into the brine and oleic phases, we use a coordinate transform to obtain the pure excess phases for the pseudo-ternary space as was proposed by Khorsandi and Johns (2018). In a transformed space excess phases are pure and the standard HLD-NAC assumptions are valid. Thus, by transferring from real ternary space into pure excess phases space we are able to model microemulsion phase behavior with surfactant partitioning. We consider oil to be immiscible in brine phase, and water to be immiscible in oleic phase.
Above CMC we perform the following coordinate transform:

$$C_{1} = \frac{C'_{1}}{1 - C'_{3w}} \qquad C_{2} = \frac{C'_{2}}{1 - C'_{3o}} \qquad C_{3} = 1 - C_{1} - C_{2} , \qquad (7)$$

where, C'_i is a true overall composition, and C_i is the transformed composition above CMC. The flash is conducted in a transformed space, where excess phases are pure. After the flash, the compositions are transformed back to real composition space:

$$C'_{1} = C_{1} (1 - C'_{3w}) \qquad C'_{2} = C_{1} (1 - C'_{3o}) \qquad C_{3'} = 1 - C'_{1} - C'_{2} \quad . \tag{8}$$

Below CMC microemulsion phase does not exists. We perform flash calculations for oleic and brine phases. We use constant partitioning K-value of surfactant for the oilbrine region. Based on mass balance and saturation equations we have three equations and three unknowns:

$$S_{w}(1-C'_{sw}) = C'_{w}$$

$$S_{o}(1-C'_{so}) = C'_{o}$$

$$S_{w}C'_{sw} + S_{o}K_{s}^{ow}C'_{sw} = C'_{s},$$

by solving the above system of equations, we arrive at:

$$S_{w} = \frac{C'_{w}}{1 - C'_{sw}},$$

$$S_{o} = 1 - S_{w},$$

$$\frac{C'_{w}}{1 - C'_{sw}}C'_{sw} + K_{s}^{ow}C'_{sw} - K_{s}^{ow}C'_{sw}\frac{C'_{w}}{1 - C'_{sw}} - C'_{s} = 0.$$
(9)

We then solve for C_{sw} in the last quadratic equation and back-calculate the remaining of the compositions and saturations. The solution for the above quadratic is:

$$C'_{sw} = \frac{\left(C'_{w} + K_{s}^{ow} - K_{s}^{ow}C'_{w} + C'_{s}\right) \pm \sqrt{\left(C'_{w} + K_{s}^{ow} - K_{s}^{ow}C'_{w} + C'_{s}\right)^{2} - 4K_{s}^{ow}C'_{s}}}{2K_{s}^{ow}}.$$

We use the root that is real and in the range of [0,1]. The above solution works for any positive (or zero) compositions. We make a flash calculation of the oil-brine phases if $C'_{3w} > C'_{sw}$ using the above equation set Eq. 9. Otherwise we calculate the microemulsion flash *above the CMC* using equations Eqs. 7 and 8.

4.2.4 Flash calculation

For microemulsion phase behavior, especially in petroleum engineering, the number of components in the system may include: a mixture of surfactants, co-solvents (alcohols), water, a mixture of salts, oil mixtures (Aarra et al., 1999). For this chapter, we combine the components into three pseudo-components: oil (nonpolar), water (polar), and surfactant (amphiphile). Such simplification allows us to calculate three-phase compositions in ternary space, given K-values at fixed temperature and pressure. Typically, K-value problems are solved using the iterative Rachford-Rice (1952) method. However, we can solve for phase compositions directly, because having three components and three-phases is a special case. The compositions are solved explicitly here using a system of linear equations, as will be discussed further.

For a three-phase system with oleic, water, and microemulsion phases, K-values are defined as follows:

$$K_i^{mw} = \frac{C_{im}}{C_{iw}} = \frac{\gamma_{iw}}{\gamma_{im}}$$
, for $i = 1, 2, 3$, for water-microemulsion phases at equilibrium.

Similarly,

$$K_i^{mo} = \frac{C_{im}}{C_{io}} = \frac{\gamma_{io}}{\gamma_{im}}$$
, for $i = 1, 2, 3$, for oleic-microemulsion phases at equilibrium,

where, γ_{ij} is an activity coefficient and C_{ij} is the volume fraction of component *i* in phase *j*. We need to define six independent K-values for coexisting three phases in equilibrium.

We construct the system of equations using phase mass balances for three phases and the definitions of six K-values. The result is in matrix form.

1	0	0	0	0	0	$-K_1^{wm}$	0	0	$\begin{bmatrix} C_{1w} \end{bmatrix}$		$\begin{bmatrix} 0 \end{bmatrix}$	
0	1	0	0	0	0	0	$-K_2^{wm}$	0	C_{2w}		0	
0	0	1	0	0	0	0	0	$-K_3^{wm}$	C_{3w}		0	
0	0	0	1	0	0	$-K_1^{om}$	0	0	C_{1o}		0	
0	0	0	0	1	0	0	$-K_{2}^{om}$	0	C_{2o}	=	0	,
0	0	0	0	0	1	0	0	$-K_3^{om}$	C_{3o}		0	
1	1	1	0	0	0	0	0	0	C_{1m}		1	
0	0	0	1	1	1	0	0	0	C_{2m}		1	
0	0	0	0	0	0	1	1	1	$\lfloor C_{3m} \rfloor$		1	
_								_				

Typical assumptions of pure excess phases in microemulsion systems provides four K-values out of six (Torrealba and Johns, 2018):

1. No oil in aqueous phase $C_{2w} \cong 0$, $K_2^{wm} = \frac{C_{2w}}{C_{2m}} \cong 0$,

2. No water in oleic phase $C_{1o} \cong 0$, $K_1^{om} = \frac{C_{1o}}{C_{1m}} \cong 0$,

- 3. No surfactant in oleic phase $C_{3o} \cong 0$, $K_3^{om} = \frac{C_{3o}}{C_{3m}} \cong 0$,
- 4. No surfactant in aqueous phase $C_{3w} \cong 0$, $K_3^{wm} = \frac{C_{3w}}{C_{3m}} \cong 0$,

The system of equations simplifies to the following:

$$\begin{bmatrix} K_1^{mw} & 0 & -1 & 0 & 0 \\ 0 & K_2^{mo} & 0 & -1 & 0 \\ 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 1 & 1 \end{bmatrix} \begin{bmatrix} C_{1w} \\ C_{2o} \\ C_{1m} \\ C_{2m} \\ C_{3m} \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 1 \\ 1 \\ 1 \end{bmatrix},$$

from the above equations $C_{1w} = 1$ and $C_{2o} = 1$, i.e. aqueous phase is pure water and oleic phase is pure oil. So, the above system simplifies to:

$$K_1^{mw} = \frac{C_{1m}}{C_{1w}} = C_{1m}$$
 and $K_2^{mo} = \frac{C_{2m}}{C_{2o}} = C_{2m}$. (10)

For microemulsion phase flash calculation we need K_2^{mo} and K_1^{mw} as a function of temperature, pressure, oil type, and any other formulation variable. For type III, both K_2^{mo} and K_1^{mw} are relevant. The microemulsion composition can be calculated as:

$$C_{1m} = K_1^{mw}$$
, $C_{2m} = K_2^{mo}$, $C_{3m} = 1 - K_2^{mo} - K_1^{mw}$.

For type II-, equilibrium is established between water-rich microemulsion and oleic phase. Therefore, only K_2^{mo} is applicable for type II- lobe. K_1^{mw} is not needed because there is no brine phase in the type II- system. Moreover, the oleic phase composition is specified (pure oil), and all water and surfactant amounts are in the microemulsion phase. This makes water to surfactant ratio from the overall composition to be the same as the microemulsion water to surfactant ratio. With known $K_2^{mo}(2^{\phi-1})$ one can calculate microemulsion phase composition as follows. The equations are derived based on K-value definition, mass balance, and tie-line information from the overall composition C_i :

$$C_{2m} = K_2^{mo~(2\phi)}, \qquad C_{1m} = \frac{1 - K_2^{mo~(2\phi)}}{\frac{C_1}{C_3} + 1} \quad \frac{C_1}{C_3}, \qquad C_{3m} = 1 - C_{1m} - C_{2m}.$$

Similarly, for type II+, equilibrium is established between oil-rich microemulsion and aqueous phase (pure water), so only K_1^{mw} is applicable. Again, we previously assumed pure excess phases, so oil-to-surfactant ratio from the overall composition is same for equilibrated microemulsion oil-to-surfactant ratio. With known $K_1^{mw}(2\phi+)$ one can calculate the microemulsion phase composition as:

$$C_{1m} = K_1^{mw \ (2\phi^+)}, \qquad C_{2m} = \frac{1 - K_1^{mw \ (2\phi^+)}}{\frac{C_2}{C_3} + 1} \frac{C_2}{C_3}, \qquad C_{3m} = 1 - C_{1m} - C_{2m}.$$

After we calculate the microemulsion phase composition for any of the microemulsion types, we proceed to calculate phase saturations from a component mass balance:

$$S_m = \frac{C_3}{C_{3m}},$$
 $S_w = C_1 - S_m C_{1m},$ $S_o = C_2 - S_m C_{2m}.$

To the best of our knowledge, this is the first time when explicit K-values are used for microemulsion flash calculation, in the context of pure excess phases. Below we present the flow chart that outlines the flash calculation algorithm. Phase behavior Type identification is same as discussed in Chapter 3. In the next section, we present phase behavior calculations for the limiting case of constant K-values where chemical potentials are independent of overall composition. Moreover, we present the procedure of how to calculate K-values for three- and two-phase (see Fig 4.3).



Fig 4.3 Flash calculation algorithm.

Three-phase K-value calculations

The phase compositions for type III phase behavior can be solved directly from the HLD-NAC equations (these are just a rewritten form of the prior net and average curvature equations),

$$\sigma_o^{3\phi} = -\frac{2}{3I(\mathcal{H} - \mathcal{H}^l)}, \qquad \sigma_w^{3\phi} = \frac{2}{3I(\mathcal{H} + \mathcal{H}^l)}, \qquad (11)$$

where $\mathcal{H}^{l} = 2/\xi_{D}^{3\phi}$, *I* is dimensionless interfacial volume ratio parameter, $\sigma_{i}^{3\phi}$ is volume of water (or oil) solubilized per volume of surfactant (solubilization ratio). See Ghosh and Johns (2016b) and Khorsandi and Johns (2016) for derivation details. The type III region exists when $|\mathcal{H}| < \mathcal{H}^{l}$ and the three-phase width in terms of HLD is only dependent on the dimensionless characteristic length of the micelles in our model (see Ghosh and Johns 2016b). This calculation is trivial. That is, $\sigma_{o}, \sigma_{w} = f(\mathcal{H}, \xi_{D}^{3\phi}; I)$ where the *I*-ratio is taken to be a constant for changing HLD and overall composition. This assumption of constant *I*-ratio is comparable to the standard cubic EOS, where there are two temperature dependent parameters (alpha and beta in Sandler (2006) notation), but one of them is fixed, while the alpha parameter is taken to be a function of temperature. Three-phase microemulsion phase behavior is successfully modeled by HLD-NAC based models and variable characteristic length proposed in Chapter 3 (Ghosh and Johns, 2016a, Jin et al., 2015, Khorsandi and Johns, 2016). Surfactant mixtures can also be used in HLD-NAC models, if the collective single pseudocomponent properties are known for the mixture (Magzymov et al., 2016). We use pure excess phases composition solubilization ratios. We can express K-values as a function of solubilization ratios.

$$K_{1}^{mw} = \frac{\sigma_{w}^{3\phi}}{1 + \sigma_{w}^{3\phi} + \sigma_{o}^{3\phi}}$$
$$K_{2}^{mo} = \frac{\sigma_{o}^{3\phi}}{1 + \sigma_{w}^{3\phi} + \sigma_{o}^{3\phi}}.$$
(12)

For the calculation of the three-phase K-values we need to have an estimate of the three-phase characteristic length, $\xi_D^{3\phi}$, discussed in the previous Chapter 3.

Two-phase K-value calculations

Two-phase tie lines should be thermodynamically consistent with three-phase tie triangle. K-values are thermodynamic state functions related to partial molar Gibbs energy, so K-values in the two-phase and three-phase regions are also expected to be consistent. Therefore, we constrain K-values to be equal at the boundary between two- and three-phase regions.

The two-phase lobes have an additional constraint at the critical points. Two-phase lobes converge into single-phase points (see Fig 4.5). The critical tie line/point has zero-length, and the corresponding K-value is 1.0. For example, type II- at the critical point for the microemulsion becomes identical to the excess oleic phase. For type II- behavior the

oil component K_2^{mo} value is used. Thus, at the critical point microemulsion phase consists of pure oil $K_2^{mo} = 1$, where microemulsion and pure oleic phase become identical, i.e. definition of critical point is when two phases become identical.

We still have two constraints when a three-phase tie triangle disappears from positive ternary space: 1) unity K-value at the critical point; and 2) immiscible brine-oil limiting tie line at the base of the ternary diagram. As was assumed previously, oil and water are immiscible, so oil and water K-values are zero at the base of ternary diagram, $K_2^{mo} = 0$, $K_1^{mw} = 0$, Therefore, we interpolate between K=1 at the critical tie line and K=0 at the water-oil base tie line instead of the tie triangle K-value. There is no positive tie triangle in a compositional space when $|\mathcal{H}| > \mathcal{H}^{\prime}$.

We assume that oil and water K-values vary monotonically from a tie triangle (or oil-water base) to a critical point as a function of tie line intercept. The K-value can change from the tie triangle K-value to K=1 as the overall composition moves from the tie triangle to the critical point. We use the tie-line parameter developed by Khorsandi and Johns (2016) for the interpolation. For oil-microemulsion equilibrium (type II-) only K_i^{mo} ($^{2\phi+}$) is relevant. Similarly, only K_i^{mw} ($^{2\phi+}$) is relevant for brine-microemulsion (type II+) equilibrium. In case of three-phase equilibrium, both K_i^{mo} and K_i^{mw} are relevant. The following sets of equations are proposed for two-phase K-values for oil and water components. These calculations are represented as gray boxes in the algorithm shown in Fig 4.3. We note here that we cannot simply use tie-triangle K-value and oil-water base K-value

value for two phase lobe extrapolation of K-values into two-phase lobes (see Fig 4.5). Therefore, we do not use negative tie-triangle K-value and oil-water base K-values for positive two-phase lobe linear extrapolations. Moreover, negative tie-triangle is not verifiable because negative space is hypothetical, i.e. unphysical.

We use the tangency condition defined by Khorsandi and Johns (2016) to find a critical tie-line:

$$b_{-}^{c} = \frac{1}{1 + \sigma_{w}^{c}}.$$

The critical characteristic length should be equal to the three-phase characteristic length, $\xi_D^{3\phi}$, at $|\mathcal{H}| = \mathcal{H}^l$ limit. We also know that the b^c_- value is minimized with increasing HLD when the two-phase lobe shrinks into three-phase zone compared to more negative HLD. The two-phase lobe shrinks in size until the lobe disappears, i.e. b^c_- approaches $b^{3\phi}_-$. Therefore, in the proposed model we use the limiting condition of the intercept as follows:

$$b^{c}_{-} = b^{3\phi}_{-} + p(-H + H^{l}),$$

Or by using three-phase tie-triangle intercept:

$$b^{c}_{-} = \frac{1}{1 + \frac{\xi^{3\phi}}{6I}} + p(-H + H^{I})$$
.



Fig 4.4 Constraints on two-phase lobe sizes. Note: above black boundaries are not twophase lobes, but compositional regions within which two-phase lobes should exist. We use the assumption that K-values should monotonically approach unity K-values from tietriangle to critical points.



Fig 4.5 Oil component K-value for Type II- lobe and three phase zone as a function of tieline intercept. This plot shows monotonic trend of K-values. The data is collected for brine 1.2 wt% NaCl, n-decane, isobutanol, TRS 10-410 surfactant at 30 ^oC. (Data from Prouvost et al., 1984).

We can then calculate the corresponding oil or water K-value of each tie line between the tie triangle and critical point by power-law interpolation. Again, three-phase oil and water K-values are calculated using the HLD-NAC equations (Eqs. 10, 11). The critical point oil K-value is $K_2^{mo} = 1$ for type II-, whereas for water K-value is $K_1^{mw} = 1$ for type II+. The above functional form can be revisited based on experimental/theoretical observations, if needed. Below are the set of equations for type II- and type II+ phase behaviors.

For type II-,
$$K_2^{mo(2\phi-)} = f\left(\mathcal{H}, \xi_D^{3\phi}, \frac{C_1}{C_3}; I\right)$$
 as shown below:

$$K_{2}^{mo(2\phi-)} = K_{2}^{mo^{*}} + \left(1 - K_{2}^{mo^{*}}\right) \left(\frac{b_{z-} - b_{-}}{b_{-}^{c} - b_{-}}\right)^{n},$$

where, b_{-} is a either tie-triangle intercept or oil-water base tie line intercept depending on HLD,

$$b_{-} = \begin{cases} 1 - \frac{K_{1}^{mw}}{1 - K_{2}^{mo}} & \text{for } |\mathcal{H}| \leq \mathcal{H}_{l} \\ 0 & \text{for } |\mathcal{H}| > \mathcal{H}_{l} \end{cases},$$

Oil K-value between microemulsion and oil is either tie-triangle K-value or oil-water boundary K-value depending on HLD:

$$K_2^{mo^*} = \begin{cases} K_2^{mo} & \text{for } |\mathcal{H}| \leq \mathcal{H}_l \\ 0 & \text{for } |\mathcal{H}| > \mathcal{H}_l \end{cases}.$$

Type II- two-phase lobe critical point intercept is

$$b_{-}^{c} = \frac{1}{1 + \frac{\xi_{D}^{3\phi}}{6I}} + p\left(-\mathcal{H} + \mathcal{H}_{l}\right).$$

Tie-line parameter defined for overall composition is $b_{z-} = \frac{C_3}{C_1 + C_3}$.

Similarly, for type II+
$$K_1^{mw(2\phi+)} = f\left(\mathcal{H}, \xi_D^{3\phi}, \frac{C_2}{C_3}; I\right)$$
 as shown below

$$K_1^{mw(2\phi+)} = K_1^{mw} * + \left(1 - K_1^{mw} *\right) \left(\frac{b_{z+} - b_{+}}{b_{+}^{c} - b_{+}}\right)^n,$$

where, b_{+} is a either tie-triangle intercept or oil-water tie-line intercept depending on HLD,

$$b_{+} = \begin{cases} 1 - \frac{K_{2}^{mo}}{1 - K_{1}^{mw}} & \text{for } \mathcal{H} \leq |\mathcal{H}_{l}| \\ 0 & \text{for } \mathcal{H} > |\mathcal{H}_{l}| \end{cases},$$

Water K-value between microemulsion and water phases is either tie-triangle K-value or oil-water boundary K-value depending on HLD:

$$K_{1}^{mw} = \begin{cases} K_{1}^{mw} & \text{for } \mathcal{H} \leq |\mathcal{H}_{l}| \\ 0 & \text{for } \mathcal{H} > |\mathcal{H}_{l}| \end{cases},$$

Type II+ two-phase lobe critical point intercept is

$$b_{+}^{c} = \frac{1}{1 + \frac{\xi_{D}^{3\phi}}{6I}} + p\left(\mathcal{H} + \mathcal{H}_{l}\right),$$

Tie-line parameter defined for overall composition is $b_{z+} = \frac{C_3}{C_2 + C_3}$.

The tuning parameters are n, p. The tuning parameters have the following functionality. The parameter n determines power-law interpolation of relevant K-values between the tie triangle and critical point. K-values are interpolated as functions of tie line intercepts. We suggest starting from n = 1, which corresponds to linear interpolation. The parameter p controls critical tie-line intercept as a function of HLD. We suggest starting from p = 0, and then increasing value of p for tuning of the phase behavior data.

Fig 4.6 demonstrates general features and limiting cases generated by the proposed model. The illustrated synthetic phase behavior changes from equal surfactant affinity to more hydrophilic surfactant conditions. From a to b, we see that type II- two-phase lobe grows (blue), and critical tie line of type II- *opens up* as HLD decreases. Type II+ two-phase lobe shrinks (red), and type II+ critical tie line *comes closer* to the tie-triangle side. As surfactant becomes more and more hydrophilic (b to c), the tie triangle disappears and the type II+ critical tie lines merges into a disappearing tie-triangle side. As we transition from b to c, three-phase tie triangle completely disappears and type II- two-phase lobe continues to grow. From c to d, surfactant becomes hydrophilic enough that the type II- critical tie line moves beyond positive ternary space with decreasing HLD, i.e. as surfactant

becomes more hydrophilic. The surfactant becomes partially miscible with oil on the oilsurfactant side of the ternary space. From d to e, surfactant becomes highly hydrophobic such that surfactant becomes completely immiscible with oil.

So far in this chapter, we presented new constraints on two-phase lobes modeling, and updated algorithm for microemulsion phase behavior modeling which has the following features:

- 1. Two-phase lobes are constrained by two physical limits: critical point and constant K-value;
- 2. Three-phase zone is consistent with HLD-NAC model;
- 3. Two-phase zone emerges from a zero-length critical tie line at \mathcal{H}_l ;
- 4. Two-phase lobes are continuous;
- 5. At extreme HLD limits, two-phase lobes grow, approaching immiscible two-phase limiting case.



Fig 4.6 Illustration of how the critical tie-line intercept approaches the three-phase tietriangle intercept $(a \rightarrow b \rightarrow c)$ with increasing HLD, and how the critical tie-line intercept diverges from a newly emerging two-phase lobe $(c \rightarrow b \rightarrow a)$ with decreasing HLD.



Fig 4.7 Synthetic phase behavior diagrams generated by the proposed model for various HLD: a. $\mathcal{H} = 0$; b. $\mathcal{H} = -0.7$; c. $\mathcal{H} = -2$; d. $\mathcal{H} = -5$; e. $\mathcal{H} = -99$.

4.3 Results and Discussion

4.3.1 Limiting case of constant K-values

We need to know oil and water K-values to model three-phase regions with constant K-values. Given K_2^{mo} and K_1^{mw} , one can construct the three-phase zone and two-phase lobes in pseudo-ternary compositional space. At the limiting case of constant K-values, each tie line in type II- and type II+ has same K_2^{mo} and K_1^{mw} , respectively. Therefore, two-phase lobes are always separated by 60 degrees angle in a pseudo-ternary space (see Fig 4.7). Constant K-values are the limiting case where the equilibrium between phases for each component is independent of the overall composition. Constant K-value constraints can be used to prevent two-phase overlapping in microemulsion phase behavior modeling (see following sections).

The results for constant K-value constraints are shown in Fig 4.7. The two-phase lobe constraints are relevant when three phases coexist in ternary space (see Fig 4.7 a and b). The brine phase disappears when the K-value of water between brine and microemulsion approaches $K_1^{mv} = 1$ (see Fig 4.7c). For a more hydrophilic surfactant, the water becomes more soluble in the microemulsion phase (see Fig 4.7 a -> b). The amount of water-solubility in the microemulsion phase increases until microemulsion and aqueous phases become identical at $K_1^{mv} = 1$ (see Fig 4.7 b -> c). Under constant K-value constraints two-

phase lobe constraints apply when the tie triangle exists in a positive compositional space. The constraints are not applicable when tie triangle disappears.



Fig 4.8 Illustration of constant K-value constraints on two-phase lobes: a. symmetric surfactant has an equal affinity to both oil and water, b. surfactant is more hydrophilic, and microemulsion is similar to aqueous phases, c. microemulsion and aqueous phase become identical, as the three-phase zone disappears.

4.3.2 60 degree constraint between two-phase lobes for real and transformed compositional space

We transform compositional space using coordinate transform to see how the K-values are affected:

$$A \times B = C$$

where, *A* is the matrix for pure oil and water pseudocomponent compositions (apex of pink ternary diagram on Fig 4.8 a), *B* is the matrix for transformed compositions (Fig 4.8 b), and *C* is the matrix for real compositional space (Fig 4.8 a):

$$A = \begin{bmatrix} 1 - C'_{3w} & 0 & 0 \\ 0 & 1 - C'_{3o} & 0 \\ C'_{3w} & C'_{3o} & 1 \end{bmatrix}_{A}, \qquad B = \begin{bmatrix} z_{1w} & z_{1o} & z_{1m} \\ z_{2w} & z_{2o} & z_{2m} \\ z_{3w} & z_{3o} & z_{3m} \end{bmatrix}_{B}, \qquad C = \begin{bmatrix} 1 - C'_{3w} & 0 & C'_{1m} \\ 0 & 1 - C'_{3o} & C'_{2m} \\ C'_{3w} & C'_{3o} & C'_{3m} \end{bmatrix}_{C},$$

where, z_{ij} is the transformed composition from real space to pure excess phases space (from Fig 4.8 a to b). Solving for transformed coordinate space gives us information about the transformed K-values:

$$B = \begin{bmatrix} z_{1w} & z_{1o} & z_{1m} \\ z_{2w} & z_{2o} & z_{2m} \\ z_{3w} & z_{3o} & z_{3m} \end{bmatrix}_{B} = \begin{bmatrix} 1 & 0 & \frac{C_{1m}}{1 - C_{3w}} \\ 0 & 1 & \frac{C_{2m}}{1 - C_{3o}} \\ 0 & 0 & 1 - \frac{C_{1m}}{1 - C_{3w}} - \frac{C_{2m}}{1 - C_{3o}} \end{bmatrix}$$

In transformed space again constant K-values correspond to transformed microemulsion composition:

$$k_1^{mw} = \frac{c_{1m}}{c_{1w}} = \frac{C_{1m}}{1 - C_{3w}}$$
 and $k_2^{mo} = \frac{c_{2m}}{c_{2o}} = \frac{C_{2m}}{1 - C_{3o}}$.

We see that actual oil or water K-values remain unchanged in both real and transformed compositional spaces. The phase diagram in Fig 4.8 demonstrates the two-phase constraints in real and transferred space. Two-phase zones constraints are separated at 60 degrees in a ternary space for both partitioning and non-partitioning surfactant cases, as was shown in the above K-value equations. Constraining K-values are directly calculated from tie-triangle compositions.



Fig 4.9 Two-phase constraints: a. real ternary space; b. transformed ternary space. Black lines are two-phase constraints based on constant K-values and critical tie lines; pink triangle represents transformed space in a real ternary space. K-values constraints on two phase lobes are separated by 60 degrees in both pure and impure excess phases.

4.3.3 Two-phase K-values and characteristic length

We first show that the proposed K-value approach is a more accurate representation of two-phase microemulsion compositions, compared to Khorsandi and Johns (2016) characteristic length approach for two-phases (see Fig 4.12, Fig 4.13, Fig 4.14). From the Figs. 4.12, 4.13, 4.14, the proposed model captures the general trends of microemulsion compositions more accurately in terms of corresponding K-values compared to Khorsandi and Johns (2016). As expected, oil and water K-values for two-phase microemulsions monotonically vary and approach a critical point (see parts a of Fig 4.12, Fig 4.13, and Fig 4.14). Besides improved accuracy the proposed K-values can be measured directly, whereas characteristic length is a hypothetical length that cannot be measured physically, except by inferring from solubility data.

Acosta et al. (2003) and Khorsandi and Johns (2016) relate surface curvature to the size of oil and water domains in microemulsion phase. The characteristic length can only be calculated from the assumption of hypothetical oil and water micelle of a spherical shape. However, for two-phases only one curvature is meaningful with dispersed spheres (see Fig 4.15).



Fig 4.10 Microemulsion composition experimental data expressed as a function of a tieline parameter for: a) Proposed K-values model; b) Characteristic length correlation (Khorsandi and Johns, 2016). Blue squares represent experimental data, red lines are corresponding correlations. Red squares on plot a) are the origin and extrapolated critical tie line for the proposed model. The data is collected for brine 0.44 wt% NaCl, n-decane, isobutanol, TRS 10-410 surfactant at 30 $^{\circ}$ C. Data from Prouvost et al. (1984), .



Fig 4.11 Microemulsion composition experimental data expressed as a function of a tieline parameter for: a) Proposed K-values model; b) Characteristic length correlation (Khorsandi and Johns, 2016). Blue squares represent experimental data, red lines are corresponding correlations. Red squares on plot a) are the origin and extrapolated critical tie line for the proposed model. The data is collected for brine 1.85 wt% NaCl, n-decane, isobutanol, TRS 10-410 surfactant at 30 ^oC. Data from Prouvost et al. (1984).



Fig 4.12 Microemulsion composition experimental data expressed as a function of a tieline parameterfor: a) Proposed K-values model; b) Characteristic length correlation (Khorsandi and Johns, 2016). Blue squares represent experimental data, red lines are corresponding correlations. Red squares on plot a) are the origin and extrapolated critical tie line for the proposed model. The data is collected for brine 0.2 wt% NaCl, oil (80vol% n-heptane, 10vol% Benzene, 10% Toluene), Tergitol 15-S-7 surfactant at 25 ^oC. Data from Bera et al. (2011).

Curvature of a sphere is defined as an inverse of the sphere radius. From Acosta et al. (2003) the definition the *average curvature* for microemulsion is the average of solubilized oil and solubilized water hypothetical spheres (also used in Khorsandi and Johns, 2016). However, in type II+ solubilized oil is irrelevant to a curvature of an interface, because there are no oil spheres in type II+, i.e. no oil curvature (see Fig 4.15). Therefore, we likely see that two-phase characteristic length are not correlated well within two-phase (see Fig 4.12, Fig 4.13, and Fig 4.14).

In the context of a two-phase microemulsion, we propose equilibrium K-values to be considered for two-phase lobes, instead. The type II+ K-value is an equilibrium of water pseudocomponent between the microemulsion and aqueous phases, K_1^{wm} . Physically, this K-value represents how well surfactant in the microemulsion is able to accommodate the water pseudocomponent inside of the microemulsion phase compared to water in the aqueous phase. Another advantage of K-values over the two-phase characteristic length is the fact that the tie-line K-value is unity at the critical point, compared to unknown characteristic lengths. Two-phase characteristic lengths at the critical point is not measurable. These arguments may be the reasons why K-values are better correlated in two-phase lobes compared to the Khorsandi and Johns (2016) approach (see Fig 4.12, Fig 4.13, and Fig 4.14).



Fig 4.13 Illustration of typical water in oil microemulsion in equilibrium with the excess brine phase. A red solid line represents an interface between microemulsion and excess aqueous phases, while black line is a boundary between oil and water domains within the microemulsion phase.



Fig 4.14 Microemulsion phase behavior modeling using the proposed model. Solid lines represent model results, dashed lines are tie lines, and squares represent experimental data: a. 0.44 % wt NaCl; b. 1.2 % wt NaCl; c. 1.85 % wt NaCl. Data from Prouvost et al. (1984).

Fig 4.14 gives results generated by the proposed model that closely match experimental data. Moreover, we see that for all cases tie lines in the two-phase regions become shorter, as the composition approaches the critical point. The experiments also show that the longest tie line is an immiscible oil and water tie line at the base of the ternary space. We also see that two-phase lobes are separated from each other at the angle larger than sixty degrees in ternary space. So, the constant K-value constraint on the size of the two-phase zone is honored.

The data in Fig 4.15 is for water – ethoxylated alcohol (surfactant) – n-alkane system where weight fractions at 25 0 C and ambient pressure were measured by gas liquid chromatography (Kilpatrick et al., 1986). The compositional data was converted to volume fractions using alkane densities from Diaz Pena and Tardajos (1978). We assume equal densities for water and surfactant.

The results show that the tuned model matches experimental data for n-hexane, noctane, n-nonane, and n-decane. Moreover, the model also predicts water-alcoholtetradecane phase behavior based on the tuned data. We see prediction in Fig 4.15e is physically valid and honors the expected behavior. For example, type II- lobe continues to grow as the surfactant affinity becomes more hydrophilic with increasing alkane chain length (decreasing HLD). Moreover, surfactant and oil become more immiscible as the oil carbon number increases (surfactant is more hydrophilic). The surfactant partitions more into the aqueous phase and less into the oleic phase as the oil carbon length increases (decreasing HLD).



Fig 4.15 Phase behavior experimental data and modeling, oil alkane scan for water/ethoxylated alcohol (surfactant)/ n-alkane system : a. n-hexane; b. n-octane; c. n-nonane; d. n-decane; e. n-tetradecane. Tuned results are in a, b, c, d, and predicted results are in e. Data from Kilpatrick et al. (1986).

Overall, the model accurately captures experimental data and adequately predicts microemulsion phase behavior. The main assumptions here were immiscible oil and water, constant partials for HLD functional form, constant partials for characteristic length $\xi_D^{3\phi}$ functional form, constant interfacial volume ratio (1), no liquid-crystals/gels/precipitation or other complex phase behaviors. If these assumptions are expected to change in the experimental data of the interest, one should make the adjustment to the model. In this chapter, we did not attempt to match all experimental data but rather to demonstrate the physical constraints, limiting conditions, K-value monotonic correlation for two-phase lobes, and general agreement to the experimental data. If more accurate matching of experimental data is desired, one may, for example, use $\left[n^{2\phi-}, p^{2\phi-}\right]$ for type II- and $\left[n^{2\phi+}, p^{2\phi+}\right]$ for type II+ to match corresponding two-phase lobes more accurately. Moreover, [n, p] parameters can be made function of other parameters like HLD, so that the phase behavior can be matched better. However, that will require additional tuning parameters and model can be overfitted with the lack of predictive capabilities.

Table 4.1	Parameters	used in	proposed	model	to generate	phase	diagrams
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Inputs	Fig 4.7	Fig 4.9	Fig 4.14	Fig 4.15
H	see figure	0	$\ln \frac{S}{1.24}$	-0.473(EACN - 8.7)
$1/\xi_D^{\max}$	0.833	0.833	$0.133 + 0.167 \ln \frac{S}{1.24}$	0.24 + 1.15(EACN - 8.7)
Ι	0.2	0.2	0.2	2.9
n	2	2	1	2
р	0.1	0.1	0.58	$p^{2\phi-} = 0.15$
				$p^{2\phi+} = 1$
C_{3w}	0	0.1	0	$0.135 \exp\left(-\frac{\mathcal{H}}{2}\right)$
<i>C</i> ₃₀	0	0.05	0	$0.135 \exp\left(\frac{\mathcal{H}}{2}\right)$

4.4 Chapter 4 conclusions

In this chapter, we presented a microemulsion phase behavior equation-of-state for all Winsor types. The microemulsion phase behavior is improved in the following ways. First, HLD concept is discussed in terms of Gibbs phase rule. Second, two-phase lobe constraints are proposed. Fourth, K-value flash calculation algorithm is proposed. Fourth, oil-water region flash calculation and surfactant partitioning model are presented in this chapter.

The following additional conclusions are made:

- Two-phase lobes are constrained to exist within two limiting conditions: tie triangle K-value and critical tie line boundary.
- 2. Two-phase lobes are constrained to be separated by at least 60 degrees in both real and transformed compositional spaces.
- 3. K-values are more suitable to model two-phase lobes, compared to using two-phase characteristic length. K-values show monotonic trends. K-values are physical compositional parameters that can be measured directly compared to hypothetical two-phase characteristic length that is inferred from the data.
- 4. Oil and water K-values remain invariant for real and transformed compositional spaces.
4.5 Chapter 4 nomenclature

Symbols	Description					
$K_i^{lphaeta}$	Equilibrium constant of component <i>i</i> between phases α and β , <i>i</i> =1,2,3					
C'_i	Overall volume fraction of pseudocomponent i , $i = 1, 2, 3$, water, oil, surfactant					
C'_{ij}	Volume fraction of pseudocomponent <i>i</i> in phase $j = w, o, m$, water, oil, microemulsion					
C_{ij}	Transformed volume fraction of pseudocomponent <i>i</i> in phase $j = w, o, m$					
\mathcal{H}	Hydrophilic-lipophilic deviation (HLD)					
V	Formulation variable, such as temperature, pressure, and composition					
S	Salinity (wt%)					
K	Partial derivative of HLD w.r.t. oil type					
EACN	Oil pseudocomponent – equivalent alkane carbon number					
α	Partial derivative of HLD w.r.t. temperature (${}^{o}C^{-1}$)					
T	Temperature (${}^{o}C$)					
β	Partial derivative of HLD w.r.t. pressure (atm ⁻¹)					
Р	Pressure (atm)					
ref	Reference state					
$\xi_D^{3\phi}$	Dimensionless three-phase characteristic length					
$\lambda_{_{v}}$	Partial derivative of three-phase characteristic length w.r.t. formulation variable					
a	Surfactant partitioning tuning coefficient					
S_{j}	Saturation of phase <i>j</i>					
C_i	Transformed volume fraction of component <i>i</i>					
$\sigma^{_{o/w}}_{_{o/w}}$	Solubilization ratio of oil or water (ratio of oil or water volume per surfactant volume)					
Ι	Interfacial volume ratio parameter					
\mathcal{H}^{l}	HLD limit of existing positive three-phase region					
$b^c_{\scriptscriptstyle -/+}$	Critical point intercept of type II-/II+ two-phase lobe					
р	Tuning parameter for critical tie line intercept as a function of HLD					
n	Tuning parameter for power-law interpolation of two-phase K-values					
$b_{_{-/+}}^{z}$	Overall composition tie line intercept					
<i>b</i>	Tie triangle (or water-oil base) intercept					
$k_i^{lphaeta}$	K-value of transformed compositions					
C_{ij}	Compositional parameters for coordinate transformation					

Chapter 5 Compositional-Dependent Viscosities in Microemulsion Systems

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Chapter Summary

Accurate estimates of compositional-dependent microemulsion viscosities are critical to model flow in surfactant-polymer floods. Microemulsions are mixtures of oil, water and surfactant with complex internal structures and interaction forces between components. This chapter develops a physics-based microemulsion viscosity model at low shear rate for compositional variations within a fixed ternary surfactant-brine-oil system. Our proposed model generates continuous viscosities for the entire compositional space with honored physical limits. First, binary water-surfactant and oil-surfactant viscosities variations along the axes of the ternary diagram are captured. Second, viscosity peaks at the "percolation locus" are reproduced, where the percolation locus is defined by hypothetical single-phase compositions within the ternary diagram. Last, end-point viscosities of pure water and oil on the apex of the ternary diagram are honored. The results show that the new model fits and predicts single phase microemulsion viscosities in ternary compositional space with acceptable accuracy ($R^2 > 0.75$) for a challenging three

pseudocomponent system of isooctane, decane, and cyclohexane mixed with water and surfactant. The first-of-its-kind viscosity model can be coupled with any microemulsion phase behavior equations of state, such as that based on HLD-NAC.

5.1 Introduction

Significant oil remains trapped in porous media after conventional water flooding due to capillary forces between oil and water (Lake et al., 2014). The addition of a predesigned surfactant component to the injected fluid can cause ultralow interfacial tension between oil and water and mobilize oil trapped by capillary forces (Bourrel and Schechter, 2010).

One important parameter that controls effectiveness of the oil recovery process is the mobility ratio, which is a function of fluid viscosities and relative permeabilities (Buckley and Leverett, 1942). The viscosity of a surfactant-oil-water system is governed by species interactions, flow conditions, and phase behavior (Paul and Moulik, 2000). Winsor (1948) first characterized microemulsion phase behavior for low surfactant concentrations: 1) dispersed oil in continuous water microemulsion in equilibrium with excess oil (type II-); 2) dispersed water in continuous oil in equilibrium with excess water (type II+); 3) mid-phase microemulsion in equilibrium with excess water (type III); and 4) single phase microemulsion (type IV). The microemulsion phase behavior depends on salinity, temperature, surfactant structure, cosolvent, oil composition, pressure, and overall composition (Healy et al., 1976, Bennett et al, 1982, Skauge and Fotland, 1990, Naceur et al., 2012). Surfactant-oil-water systems may also form gels, liquid crystals, and other undesired phases that are avoided for enhanced oil recovery applications (Moulik and Paul, 1998, Hirasaki et al., 2008).

Microemulsion viscosity can reach undesirably high values at certain compositions (Hirasaki et al., 2008), while also giving low viscosity near optimal solubilities (Bennett et al., 1982). High viscosities can cause unfavorable mobility ratios and injectivity problems in the field. The optimum salinity corresponds to a minimum in the interfacial tension (IFT), which is decreased the most at high solubilities of oil and brine into the microemulsion phase (Huh 1979). The chemical design must achieve ultra-low IFTs, while also avoiding excessively large viscosities. This is normally designed in the lab based on a few experiments, where viscosities are matched using empirical functions. These empirical functions are then fixed and input into chemical flooding simulators, which are used to predict oil recovery from surfactant flooding. The fixed viscosity models, however, cannot account for physical changes in viscosities as parameters vary away from the experimental data set used for tuning.

Observations of measured microemulsion viscosities reveal complicated trends. Commonly, experimental measurements of both phase behavior and viscosities are made where salinity changes, but overall composition of oil, brine, and surfactant is kept fixed. As salinity increases, the anionic surfactant affinity shifts towards oil, which shifts the phase behavior toward type II+. A different set of viscosity data would result, however, for different overall compositions.

Ideally, phase behavior and viscosity would be measured for changing composition, and other formulation variables such as temperature and pressure. But such experiments are scarce in the literature. Nevertheless, some key features of viscosity behavior can be deduced that are closely related to a change in structure. For example, at high oil compositions, micelles form with dispersed water and surfactant at the interface. As the fraction of water increases, micelles change shape, form clusters or coalesce into larger micelles (Davis, 1994). The increase in the fraction of the dispersed domain, along with the change of shape and possible elongation of micelles, results in a larger mixture viscosity, as has been observed and modeled in suspensions and emulsions (Einstein 1906, Taylor 1932, Roscoe 1952, Mooney 1951, Krieger and Dougherty 1959, Simha, 1950).

There usually is a threshold at which conduits of secondary component form, leading to the formation of two continuous domains of oil and water. This threshold is known as the percolation threshold. Many observations indicate that this threshold is responsible for the observed viscosity peaks (Peyrelasse and Boned, 1990, Mathew et al., 1991). At larger concentrations than the percolation threshold, larger fractions of secondary component become continuous. Bicontinuity, as defined here, usually coincides with a decrease in viscosity (Peyrelasse et al., 1988). The fully continuous domain reverses at a certain composition, where the microstructure at this composition resembles a sponge-like shape, in that the two domains are fully continuous while intertwined. There is also a composition at which viscosity reaches a local minimum, which according to Bennett (1985) correlates well with the point of equal concentration of oil and water. Khodaparast and Johns (2018) conjectured that this local minimum in viscosity occurs at domain inversion: the microemulsion will reach a state of full continuity for both domains, where there is no disconnected dispersion of one domain found in the other.

Models that describe the viscosity of liquids containing inclusions are mostly limited to one fully discontinuous domain (particles or droplets) and another fully continuous one. Einstein was first to theoretically derive a relationship of the effective viscosity of a dilute suspension of rigid spherical particles as a function of volume fraction of those spherical particles (Einstein 1906), in which viscosity increases with volume fraction. Semi-dilute and concentrated suspensions have even larger increases in viscosity. Mooney (1951) provided a phenomenological proof that suspension-to-matrix viscosity ratio can be modeled by an exponential function of particle volume fraction. Roscoe (1952) used a power law following similar reasoning. Krieger and Dougherty (1959) proposed a power function that diverges to infinite values at a specific volume fraction of dispersed particles dubbed as the maximum packing fraction, owing to the rigidity of suspended particles. The maximum volume fraction changes depending on the favored packing (Gradzielski and Hoffman 1999). However, in the case of microemulsions, the rapid increase does not diverge to very large values owing to the onset of bicontinuity and formation of conduits of another liquid domain. A viscosity of co-continuous mixtures has

also been examined (Heitmiller et al., 1964, Lin 1979, Utracki et al., 1982), in which the models usually consider full continuity of both components at any fraction.

Existing microemulsion viscosity models implement one or more of the models mentioned above to capture viscosity behavior (Quemada and Langevin, 1989, Kiran and Acosta, 2010, Tagavifar et al., 2017), but fall short in reproducing at least one of the key observed features. Kiran and Acosta (2010) established a method to model changes in micellar shapes in accordance with the HLD-NAC model, but did not address the bicontinuous region viscosity. Tagavifar et al. (2017) used fluidity theory and Mooney-type exponential viscosity to address viscosity in both discontinuous and bicontinuous regions, but this approach could not generate the observed double peaks in viscosity in salinity scans. Khodaparast and Johns (2018) implemented Lin's modified version of fluidity theory combined with Roscoe's power law for effective viscosity of dispersions to capture the two peaks and the local minimum. Their model fixed the percolation threshold to two values in a pseudobinary approximation.

This chapter developed a physics-based model that captures viscosity variation in compositional space that will aid the design of chemical enhanced oil recovery. We extend the viscosity model of Khodaparast and Johns (2018) to account for all possible composition variations within a pseudoternary diagram at fixed temperature and pressure. First, we describe the coupling of viscosity to microemulsion phase behavior. Second, we develop an algorithm to generate viscosity maps (viscosity variations in ternary composition space), by proposing a model for the percolation locus in compositional space. This percolation locus is then coupled to the binary viscosity model of Khodaparst and Johns. Last, we demonstrate tuning of the model to experimental data, while reserving some data to demonstrate viscosity predictions.

5.2 Methodology

In this section we first describe the coupling approach of microemulsion phase behavior with the viscosity map. Next, we propose a percolation model in pseudoternary space based on experimental measurements in the literature. Last, we implement the new percolation model and give an algorithm to calculate viscosity that incorporates the main features of the Khodaparast and Johns model (2018).

The viscosity model utilizes microemulsion phase composition as the input for the model. Microemulsion phase behavior is a function of intrinsic properties and overall composition according to Gibbs phase rule. Prediction of microemulsion phase behavior includes empirical, theoretical and practical models (Pope and Nelson, 1978, Rossen et al., 1982, Khorsandi and Johns 2016). The model by Khorsandi and Johns (2016) was the first practical flash calculation algorithm based on HLD-NAC to solve for equilibrium phase compositions and phase amounts for all Winsor regions where temperature, pressure, oil type, surfactant structure, brine salinity, and alcohol content can vary. Thus, we use that approach to demonstrate phase behavior calculations in this chapter.

The flash algorithm generates equilibrium phase compositions at boundaries of two and three-phase regions (see Fig 5.1a, shown near optimum). Because of phase splits, experimental viscosities cannot be measured at overall compositions within these multiphase regions. Viscosities can be estimated analytically, however, for hypothetical singlephase compositions over the entire composition space, as illustrated in Fig 5.1b and discussed in the next section. As shown in Fig 5.1b, the hypothetical viscosities exhibit a peak along a locus of percolation thresholds. The percolation thresholds can intersect the phase behavior in complicated ways. The viscosities shown here ignore gels or other crystalline structures that can form at large surfactant concentrations (this is indicated by not showing viscosities in the top of the ternary diagram). Overlying these hypothetical viscosities with phase behavior gives the viscosity map of physical single-phase compositions (see Fig 5.1c).

Ideally, tuning of the viscosity model should be coupled with the phase behavior model. When a change occurs in a thermodynamic state variable such as temperature, oil type, and salinity, both phase behavior and viscosity map change simultaneously (see Fig 5.1 c to d).



Fig 5.1 Generation of a viscosity map: a.) phase behavior near optimum conditions determined from a flash calculation; b.) viscosities for hypothetical single phase microemulsion compositions; c.) intersection of phase behavior with viscosities, phase splits eliminate viscosities; and d.) viscosity map variation at over optimum conditions, e.g. increased salinity.

A microemulsion may be oil continuous, water continuous, or bicontinuous with various structures, such as lamellar, cubic, and hexagonal internal structures (Davis, 1994). Salager et al. (2002) showed that at domain inversion microemulsions become extremely viscous. According to Moulik and Paul (1998), inversion from water continuous to bicontinuous domain occurs at the approximate threshold of 80% water content, and from bicontinuous to oil continuous at around 20% water content for the studied water-AOT-decane system.

The percolation locus within the ternary space is critical to determine the compositions where viscosity peaks. Unfortunately, there is limited data to generate such a locus based solely on overall composition variations. One data set shows that the percolation threshold from conductivity experiments is well correlated with an increase in viscosity of microemulsion (Peyrelasse and Boned, 1990, Mathew et al., 1991). Fig 5.2 shows these viscosity measurements with clear viscosity peaks for the ternary mixtures of water, surfactant and three different hydrocarbons. As shown, superimposed compositional data of the locus for three different hydrocarbons follow similar trends in the ternary diagram. Thus, we propose a percolation threshold model as shown in Fig 5.2 that fits the measured data, and has symmetry with that data in the water continuous region. This follows the same interpretation of Peyrelasse and Boned (1990) in correlating viscosity peaks with percolation threshold, but they did not provide a percolation locus model.



Fig 5.2 Peaks in viscosity for microemulsion phases at 25 oC (shown by solid black points). The blue line is our model of the proposed percolation threshold locus that is tuned to the experimental data. Data from Peyrelasse et al. (1988).

The peak in viscosity of a fixed three component oil-water-surfactant system is also correlated with conductivity and permittivity percolations (Boned et al., 1993). Fig 5.3 shows conductivity percolation data for a ternary mixture of surfactant, water and undecane at three different temperatures. The trend supports the proposed percolation threshold locus.

The locus in Fig 5.3 should be a function of temperature and state variables, but owing to the complexity of conductivity percolation data, no attempts were made to fit individual temperature loci. Instead, the general trend that includes different temperatures is matched as one data set.

We propose a percolation threshold model within pseudoternary compositional space based on the general observations from the limited set of experimental data shown. The model is derived from a general quadratic equation and for simplicity is constrained to intersect the brine and oil apex:

$$\Pi_{1}C_{w}(1-C_{w}-C_{o})+\Pi_{2}C_{o}(1-C_{w}-C_{o})=C_{o}C_{w},$$
(1)

where, $C_{w(o)}$ are concentrations of water (oil); and $\Pi_{1,2}$ are positive tuning percolation parameters. For example, the parameters are $\Pi_1 = \Pi_2 = 0.19$ in Fig 5.2, and $\Pi_1 = \Pi_2 = 0.6$ in Fig 5.3. Although not used here, the presence of two tuning parameters allows for an asymmetric percolation locus. Percolation threshold is expected to vary as a function of temperature, oil composition, surfactant type. For more robust viscosity modeling, one may determine functionality of $\Pi_{1,2}$ as a function intrinsic properties through experiments and theoretical models, if needed. In this chapter, $\Pi_{1,2}$ are tuned for a specified surfactant-oilwater system with other intrinsic properties held fixed.

The proposed percolation model is not a universal solution, and other models may be used. The important idea here is to define a locus of percolation that corresponds with a change in continuity and corresponding increase in viscosity. The locus must be tuned to experimental data, and could shift as a function of temperature, pressure, and other intrinsic properties including oil type (through equivalent alkane carbon number) and salinity.

The main contribution of this chapter, therefore, is to model the impact of surfactant concentration in pseudoternary compositional space on viscosity by inclusion of a continuous percolation locus. Once a percolation locus is determined by tuning, we also account for the amount of surfactant added to oil and water for use in the Khodarapast and Johns (2018) model, in which effective pseudo oil and brine concentrations are required.

We take a different approach to generate the effective pseudo oil and brine concentrations than in Khodarapast and Johns, owing to the location of our percolation locus (which goes through the oil and brine apex). This change allows our model to match two important limiting cases at the boundaries of the ternary diagram. These limiting cases are based on the observed trends where viscosities of microemulsions with only dispersed surfactant micelles (see Wang et al., 2004 with no oil or brine) increase along the brinesurfactant and oil-surfactant axis as surfactant concentration increases.



Fig 5.3 Conductivity percolation locus measurements for undecane at three temperatures: blue line is our proposed percolation threshold locus model. Data from Moha-Ouchane et al. (1987).

The new approach is to split the surfactant volume into half and lump each half with any oil and brine present. If no oil or brine is present, then the surfactant becomes hypothetical oil or brine in pseudobinary space, allowing for an increase in microemulsion viscosity. This approach is reasonable as long as surfactant concentrations are not too large. This assumption of only two domains (oil and brine) is similar to that made by others (Safran and Turkevich, 1983, Khorsandi and Johns, 2016, Tagavifar et al., 2017). Thus, for water and oil domains:

$$C_i^{*m} = C_i^m + \frac{1}{2}C_s^m \qquad i = w, o,$$
⁽²⁾

where, C_i^m is a volumetric concentration of oil, water, and surfactant pseudocomponents in the microemulsion phase, o, w, s respectively; and C_i^{*m} is the effective pseudo oil or water domain volume fraction. Roscoe's model (1952) for suspension viscosity is then used to explain the viscosity increase due to added surfactant micelles.

Fig 5.4 illustrates important features for viscosity calculations based on the prior model of Khodarapast and Johns (2018). Their model divides the composition space into a binary structure with three main regions: water-continuous (wc), oil-continuous (oc) and bicontinuous (bc). The micelles are fully dispersed in the wc and oc regions, in that is there is no connectivity of the water domain in the oc region (similarly no connectivity for the oil domain in the wc region). The continuous domain viscosity increases due to dispersed inclusions in the continuous matrix. In the bicontinuous region, there is a degree of

continuity for both the water and oil domains depending on which domain is dominant. Continuity is determined via a normalized percolation equation (Fig 5.4 a,b), in which the remaining dispersions increase the viscosity of the dominant "fully-continuous" domain. Bicontinuous viscosity is then affected by the viscosity of both continuous domains according to a modified fluidity equation

The workflow and algorithm is summarized in Fig 5.5, where the dashed box shows the equations developed by Khodaparast and Johns (2018). The algorithm requires several inputs such as phase compositions, endpoint component viscosities (μ_i), interaction parameter (α), and percolation critical exponent (κ_i) (Lee et al., 1986), intrinsic viscosity ($[\eta_i]$), and percolation parameter (Π_i). Only the equilibrium microemulsion phase composition from flash calculations (e.g. Khorsandi and Johns, 2016, Torrealba and Johns, 2017) should be input to the viscosity model. The locus of percolation thresholds, normalized domain compositions are calculated, where a surfactant is treated as a part of the oil and water domains in the microemulsion. Based on the domain compositions, we then calculate the dispersed and continuous volume fractions as proposed by Khodaparast and Johns (2018). Dispersed volume fractions contribute to the increase of continuous domain viscosities as shown by Roscoe (1952). Last, microemulsion viscosity is calculated using Lin's (1979) model for simultaneous flow of two adjacent fluids with interfacial friction between two domains. For more details, see Khodaparast and Johns (2018).



Fig 5.4 a.) A viscosity of water-continuous (wc), oil-continuous (oc) and bicontinuous (bc) domains for a fictitious case of 1-cp water and 0.5-cp oil; microemulsion viscosity (dashed) is a combination of both as shown by the dashed green line; and b.) Parameters: variation of water-continuous volume fraction (C_{wc}), dispersed water in oil domain (C_{wd}), and dispersed oil in water domain (C_{od}). Dashed lines for both (a) and (b) indicate percolation thresholds (here $C_{w}^{*cr} = 0.2$, $C_{o}^{*cr} = 0.3$).



Fig 5.5 Proposed microemulsion viscosity calculation algorithm. The first two boxes show the equations developed in this chapter, while the large box with dashed lines show the equations from Khodarapast and Johns (2018).

5.3 Results and discussion

This section gives microemulsion phase viscosity calculations by our proposed model for a single phase system reported in Peyrelasse et al. (1988). The viscosity data used is for fixed ternary components (AOT surfactant, water, and oil), temperature, and pressure, but does allow for varying compositions in that ternary space. The volumetric composition data shows increasing water to surfactant volumetric ratio *WSR* at fixed oil fraction C_o^m . Phase splits do not occur for any of these compositions as the surfactant concentrations are large. Although it is not ideal to have such large surfactant concentrations for EOR applications, the single phase data were the best data available in the literature that give viscosities changing with composition.

Molar ratio was converted into volumetric ratio using molecular weight, assuming similar solution densities for water and surfactant (1 g/cc). There was no data on the water continuous region of the ternary diagram, so we assume symmetry of the percolation locus in the results that follow.

Fig 5.6 shows the tuned fit of the proposed model to the experimental data for microemulsion phase viscosity in compositional space for water, isooctane and Na(AOT). Table 5.1 shows the tuned values, where we kept two viscosity parameters constant with composition (κ_i and $[\eta_i]$).



Fig 5.6 Viscosity as a function of composition: oil is isooctane, surfactant is Na(AOT): a.) fit of proposed model to experimental data, and b.) overall agreement of model with experiments. The blue dashed lines with squares represent experimental data, while solid red lines are model results. The experiments given by the bold blue line was not used in tuning, while the dark red line shows its prediction from the model. Data from Peyrelasse et al. (1988).

As shown in Fig 5.6, the model with few parameters is capable of capturing the viscosity peak(s) in compositional space, where the peak is associated with percolation of the dispersed domain. The viscosity along the oil-surfactant axis (at WSR = 0) increases when the volume fraction of the dispersed domain increases, owing to the formation of reversed micelles and structures. At fixed volume fraction (C_o^m), the viscosity increases with increasing water to surfactant ratio until the percolation threshold, where water continuity is initiated (which leads to reduced dispersions of water and surfactant micelles). Thus, microemulsion viscosity decreases as its structure percolates and becomes bicontinuous. The absolute value of viscosity at the peak increases with decreasing volume fraction of oil, potentially implying a more complicated interaction between oil-watersurfactant species, such as micellar shape transitions and stronger surfactant-surfactant interactions (Davis, 1994, Mitchell et al., 1983). Nevertheless, the model captures the overall trend of viscosity in compositional space for fixed components. The model, however, does not capture well the magnitude of viscosities at larger water-to-surfactant ratio. These inaccuracies are likely related to compositional effects on κ_i and $[\eta_i]$ as is explored at the end of this section.

Fig 5.7 shows hypothetical viscosities generated by the proposed model for fixed temperature and pressure assuming only a single-phase microemsulsion. Two peaks in viscosity are attributed to the percolation from the oil-continuous to bicontinuous domains and from the bicontinuous to water-continuous domains. The figure shows that the viscosity on the water side of the compositional space is generally higher than viscosities on the oil side because the end-point water viscosity is twice that of isooctane. Owing to lack of data, it is difficult to confirm the percolation threshold locus at very low surfactant concentrations near the oil and brine axis, which is known to be a multiphase region (Moulik and Paul, 1998). We also assume here that the critical micelle concentration (CMC) is always achieved, even though we know that there is a small two-phase oil-brine region below the CMC.

Fig 5.8 and Fig 5.9 show similar results for different surfactants and oils. The viscosity model captures the experimental trends well in that viscosity peaks coincide with the percolation locus, as observed from experimental data. Also, owing to the proposed normalization in Eq. 2, as surfactant concentration increases so does the dispersed phase fraction. Therefore, viscosity increases with greater surfactant concentration near the oil-surfactant and brine-surfactant axis. As was shown previously, the peak in the viscosities are correlated with the percolation composition. However, the maximum viscosity may occur within the bicontinuous region, because dispersed domain fraction may still increase after the percolation composition (see Fig 5.4). Maximum viscosities are also observed within the bicontinuous region in Fig 5.8 and Fig 5.9 as shown by the unusual bend in the viscosity curve. This feature would likely not be detected in experiments owing to measurement errors.



Fig 5.7 Calculated hypothetical viscosities for isooctane (Tuned on data from Peyrelasse et al. 1988).

	μ_o, cp	μ_w, cp	α	ĸ	K _w	$[\eta_o]$	$[\eta_w]$	Π_1	Π_2
isooctane, NaAOT, water	0.47	1	1.1	1.9	1.9	13.6	13.6	0.19	0.19
cyclohexane, NaAOT, water	0.86	1	1.5	1.6	1.6	11.0	11.0	0.19	0.19
n-decane, Ca(AOT) ₂ , water	0.85	1	1.7	1.1	1.1	20.8	20.8	0.3	0.3

Table 5.1 Tuned parameters and inputs for the viscosity model



Fig 5.8 Viscosity as a function of composition from experimental data compared to model results: a.) oil is n-decane and surfactant is Ca(AOT)2, data from Pan and Bhatia (2008); and b.) oil is cyclohexane and surfactant is NaAOT. Data from Peyrelasse et al. (1988).



Fig 5.9 Viscosity map in compositional space from model: a.) oil is n-decane and surfactant is Ca(AOT)2, data from Pan and Bhatia (2008); b.) oil is cyclohexane and surfactant is NaAOT, data from Peyrelasse et al. (1988).

The proposed model captures the observed features in the experimental data such as viscosity peaks associated with percolation and the bicontinuous region. However, the quantitative match is objectively not perfect. Lack of precise accuracy of the model may be a result of oversimplification of the system. For example, we assume that for fixed components, the intrinsic viscosity parameter $[\eta_i]$ and percolation power exponent κ_i are constant. However, intrinsic viscosity is a function of dispersed domain structure, deformability, and orientation (Simha 1948, Taylor et al. 1931, Yamamoto and Matsuoka, 1994). Moreover, the percolation exponent is also a function of microstructural shapes, orientation, and pressure (McLachlan et al., 1990, Lee et al., 1986). The internal structure of microemulsion is a function of microemulsion phase composition, along with other state variables. Micellar shapes such as spherical, cylindrical, lamellar, bicontinuous, or other complex structures are possible in pseudoternary space (Davis 1994). Therefore, it is expected that $[\eta_i]$ and κ_i are a function of phase composition and other intrinsic properties, such as temperature.

Fig 5.10 demonstrates a possible improvement in the model accuracy. Here, we estimated the change in the percolation power exponent with composition by averaging the percolation exponent for all data with the same oil composition, while keeping all other parameters unchanged. The results in Fig 5.10a show that the mean percolation parameter κ_w is nearly a linear function with oil composition. The values obtained are physically realistic in that κ_w should be greater than 1.0 (see Appendix E). Fig 5.10b illustrates

significant improvement in viscosity estimates using the average percolation exponent κ_w for each fixed oil composition (compare to Fig 5.6a).

Ideally, model parameters such as $[\eta_i]$, κ_i , and α should be functions of microemulsion phase oil and water compositions according to the Gibbs phase rule. Although not done here, several limiting conditions should be satisfied. Intrinsic viscosity should approach a value between 1 and 2.5 for pure oil and water compositions, where micelles approach spherical shapes (Einstein, 1906, and Taylor, 1932). Further, the percolation exponent κ_w should be greater than unity (see Appendix E). According to the proposed algorithm, oil intrinsic viscosity is relevant for oil compositions above domain inversion composition (see Fig 5.4). Similar reasoning applies for the water intrinsic viscosity. Further, the oil percolation exponent is only applicable in the compositional window between the percolation threshold and domain inversion compositions.

Additional improvements are also possible beyond those shown in Fig 5.10, such as making the intrinsic viscosity a function of both the oil composition and the watersurfactant ratio. We also assumed here that surfactant contributes volume to both the oil and water domains. However, this assumption may breakdown for very large surfactant concentrations (such as the system we examined here) where accumulation of surfactant at the interface likely creates a non-negligible domain compared to the oil and water domains. Such high surfactant concentrations can also result in complex viscosity and phase behavior, such as when gels, liquid crystals, and other precipitates form (Tiddy, 1980). Therefore, we suggest to limit the application of our model to surfactant concentrations less than $C_{s\,\text{max}}^m = 1/(2(\Pi_1 + \Pi_2) + 1)$, which is the surfactant concentration at which oil and water percolation thresholds meet. Moreover, above $C_{s\,\text{max}}^m$ and along equal water-oil ratio the model will produce a sharp viscosity change from oil continuous to water continuous microemulsions because of the assumption of domain inversion at equal oil and water concentrations. The sharp change in viscosity is a consequence of the domain inversion assumption rather than what is physically expected. Therefore, the model should only be applied for surfactant concentrations below $C_{s\,\text{max}}^m$, which is reasonable for enhanced oil recovery applications that economically requires the use of a small volume of surfactant.



Fig 5.10 Improved accuracy of viscosity by making percolation critical exponent as a function of oil composition: a.) critical exponents based on individual fits of compositional scan at fixed oil fractions; and b.) improved accuracy of the proposed model. Data from Peyrelasse et al. (1988). Model inputs are $\alpha = 1.5$, $[\eta_o] = [\eta_w] = 13.5$, $\kappa_o = \langle \kappa_w \rangle$, with $\langle \kappa_w \rangle$ from Fig 5.10a.

5.4 Chapter 5 conclusions

We have developed a microemulsion viscosity model that accounts for variations in overall compositions within a ternary diagram. The model can be easily coupled with microemulsion phase behavior equations-of-state (EoS) for inclusion into chemical flooding simulators and to aid in the design of surfactant floods. The following key conclusions are made:

- The increase in viscosity with increasing surfactant concentration in pure oil and water can be explained by splitting and lumping surfactant volume into the oil and water domains, which is then modeled through Roscoe's (1952) suspension viscosity model.
- A model for the percolation locus in compositional space is given to account for the observed increases in viscosity. We assume symmetry of the percolation locus owing to lack of viscosity data in the water continuous region.
- 3. The binary model by Khodaparast and Johns (2018) is successfully extended to ternary compositions.
- 4. The new compositional viscosity model fits experimental data well and predicts the viscosity in compositional space with acceptable accuracy ($R^2 > 0.75$).
- 5. Percolation exponent is shown to vary as a function of microemulsion oil composition. The variation is the result of micellar shape transitions in compositional space. A consistent trend is observed for average percolation exponent as a function of the oil composition.

The quantitative accuracy of the model may be improved further by accounting for more physical functionality of the model parameters, such as compositional variation of intrinsic viscosity, critical percolation exponents, surfactant-rich interfacial domain contribution, and continuous domain interaction parameters with continuous oil-water-surfactant contributions. However, the model proposed here is simple and a substantial improvement over current industry models used today.

5.5 Chapter 5 nomenclature

Symbols	Description					
C_i	Overall volume fraction of species $i, i = o, w, s$, oil, water, surfactant					
$\Pi_{1,2}$	Percolation locus tuning parameters (positive values)					
μ_{m}	Microemulsion phase viscosity (cp)					
μ_{oc}	Oil-continuous domain viscosity (cp)					
$\mu_{_{wc}}$	Water-continuous domain viscosity (cp)					
$\mu_{o,w}$	Endpoint pure oil and water viscosity (cp)					
C_i^m	Volume fraction of species <i>i</i> in microemulsion phase, $i = o, w, s$					
C_i^{*m}	Effective pseudo oil (or water) domain volume fraction, $i = o, w$					
WC	Water-continuous compositional domain					
OC	Oil-continuous compositional domain					
bc	Bicontinuous compositional domain					
C_i^{*cr}	Percolation threshold for oil and water domain volume fractions, $i = o, w$					
α	Interaction parameter					
K _i	Percolation critical exponent, $i = o, w$					
$[\eta_i]$	Intrinsic viscosity					
WSR	Water to surfactant volume ratio					
C_{od}^{*m}	Dispersed oil in water pseudo domain volume fraction					
C^{*m}_{wd}	Dispersed water in oil pseudo domain volume fraction					
C_{oc}^{*m}	Continuous oil in oil pseudo domain volume fraction					
$C^{*m}_{_{\scriptscriptstyle WC}}$	Continuous water in water pseudo domain volume fraction					

Chapter 6 Modeling the Effect of Reaction Kinetics and Dispersion during Low-Salinity Waterflooding

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Chapter Summary

Wettability alteration has been recognized as the primary mechanism responsible for improved oil recovery during low-salinity waterflooding. A complex network of ionic reactions at the oil/brine/rock interfaces facilitates the alteration in wettability. The specific chemical species that govern the alteration process for both sandstones and carbonates can vary, which makes a common model challenging.

In this research, we construct a mechanistic binary model that applies to both sandstone and carbonate reservoirs and considers the impact of physical dispersion and reaction kinetics on recovery. The proposed model is based on the premise that the wetting species are known and can be lumped as either oil-wetting or water-wetting pseudocomponents. For the cases studied, the model was found to reproduce the experimental results well. Further, simulations show a significant impact of reaction kinetics on the rate of wettability alteration compared to assuming instantaneous equilibrium. For the limiting case of a slow reaction rate (Damköhler number, Da ~ 0), low-salinity injection does not alter wettability. For fast reactions (Da ~ 10^5), the ultimate oil recovery is highly sensitive to the injected fluid salinity. The wettability alteration front is delayed compared to the injected fluid because of the excess salt desorbed from the rock surface into the aqueous solution. Such a delay in wettability alteration is important when considering an appropriate slug size for the low-salinity slug. Lastly, we observed that dispersion had little effect on the ultimate oil recovery during wettability alteration as compared to reaction kinetics.

6.1 Introduction

Low-salinity waterflooding (LSWF) is a growing field of research in the energy industry largely due to its significant potential at relatively low cost. The term "lowsalinity" refers to the reduced salt concentration of the injection brine as opposed to the high-salinity formation brine utilized for waterflooding practices. Experimental research has shown the positive impact of LSWF in terms of improving oil recovery from both sandstone (Tang and Morrow 1999) and carbonate reservoirs (Zhang et al., 2007). The growing body of research has led to the implementation of the LSWF technique at field scale, for example, at North Sea, Alaska, and Minnelusa formations (Mcguire et al., 2005; Skrettingland et al., 2011; Thyne and Gamage, 2011).
Different factors have been associated with the success of LSWF (Purswani et al., 2017). These include the rock composition (Austad et al., 2012), formation and injection brine composition (Austad et al., 2005; Fathi et al., 2011a, 2010a; Zhang and Austad, 2006), crude oil composition (Fan and Buckley 2007; Fathi et al. 2010; Fathi, Austad, and Strand 2011a), and the temperature of the reservoir (Zhang and Austad 2006). Because of the diversity of these factors, there is inherent complexity in the low-salinity effect (LSE). This has led many researchers to postulate various mechanisms that explain the observed oil recovery from LSWF. There is growing consensus in that wettability alteration occurs during LSWF, which causes a change in the wetting state of the rock from oil-wet to more water-wet. This alteration in wettability has been attributed to either multi-component ion exchange (Lager et al., 2008), chemical mechanism (Zhang et al., 2007), fines migration (Tang and Morrow 1999), or double-layer expansion (Myint and Firoozabadi, 2015). These mechanisms vary for the oil/rock/brine type under consideration.

The mechanisms proposed in the literature are largely based on the competition between oil-wetting and water-wetting species that occupy the rock surface. For example, the mechanism for fines migration for wettability alteration as observed in the experimental research performed on homogeneous sandstone cores (Yildiz and Morrow 1996; Tang and Morrow 1997; Tang and Morrow 1999). It has been suggested that fine particles that exhibit mixed wetting characteristics hold oil attached to the rock surface, and then detach upon the injection of a low-salinity brine. Other researchers (Lager et al., 2008) attribute the improved oil recovery to the ionic exchange between the rock surface and the lowsalinity brine, where the variety of functional groups in crude oil are attached to the rock surface via ion/ligand bridging with the multivalent ions present in the formation water. The injection of a low-salinity brine disturbs the equilibrium established among the oil/rock/brine system, which leads to the migration of multivalent ions from the ion-bridged state toward the brine and in the process release the crude oil (Lager et al., 2008). A similar mechanism has been suggested for carbonate reservoirs based on the interactions of the potential determining ions (such as divalent Ca^{2+} , Mg^{2+} and SO_4^{2-}) present in the injection brine (Purswani et al., 2017; Purswani and Karpyn, 2019; Zhang et al., 2007; Zhang and Austad, 2006).

Alongside the growth of experimental research to understand the LSE, there have been simultaneous developments to model these experiments accurately. One of the early mathematical models was proposed by Jerauld et al., (2008). In this analytical model, wettability alteration caused by the injection of a low-salinity brine was captured through linear changes in relative permeabilities and fractional flows at two specified end-points of high- and low-salinity. Buckley-Leverett (1942) 1-D solutions were developed to account for saturation and corresponding oil recovery changes. Later, (Qiao et al., 2016, 2015) improved the model by Jerauld et al., (2008) for carbonate reservoirs by including a network of chemical reactions at the oil/water interface and between the oil/water and rock using a surface complexation approach. Their reaction network accounted for crude oil adsorption/desorption, mineral dissolution, and salt precipitation in order to predict wettability alteration (contact angle and residual oil saturation) in carbonate reservoirs, instead of using linear interpolation between end-point relative permeabilities.

Korrani and Jerauld (2019), advanced the surface complexation reaction approach by including electrostatic forces and van der Waals interactions at the oil/brine and rock/brine interfaces. These interactions were then related to wettability state using the stability of the thin water film. They coupled the geochemical modeling software (PHREEQC) with a reservoir simulator (UTCHEM) to model LSWF in both carbonates and sandstone rocks. Different experimental data sets from the literature were used to find a good match to their proposed model by tuning end-point relative permeabilities between high-salinity and low-salinity waterfloods.

LSWF heavily depends on the composition of the injected water. Dispersion of components in single-phase fluids affects compositional dependent processes, such as enriched-gas floods (Johns et al., 2002) and huff-soak-puff (Cronin et al., 2019). Dispersion alters the phase composition via several mechanisms, such as complex pore geometry, molecular diffusion, interaction of fluid and solid phases, and external forces (Bear, 1972). Al-Ibadi et al. (2019b, 2019a) showed that dispersion affects fractional flow during low-salinity waterflooding with fast reactions. However, current modeling efforts do not quantify the importance of dispersion in the brine phase combined with reaction kinetics during LSWF.

Pore (or sub-pore) scale experimental work by Mahani et al. (2015a, 2015b) and Bartels et al. (2019, 2017) have demonstrated that wettability alteration is likely a timedependent process. Mahani et al. (2015a) conducted static experiments for wettability alteration on silica substrates coated with clay (montmorillonite). It was found that the contact angle and contact area of the oil droplets changed to less-oil-wetting conditions in the presence of a low-salinity brine, which helped in weakening the adhesion forces that pin the oil droplet to the clay surface. More importantly, this LSE took several hours to complete until the droplet of oil finally detached from the surface due to buoyancy. The authors argued that both DLVO (Derjaguin, Landau, Vervey, and Overbeek) and non-DLVO based interactions explain the slow reaction rate. DLVO-based interactions include the slow electrokinetic diffusion of ions in the thin water film between the oil and clay Non-DLVO-based interaction, however, includes ion-bridging or chemical surface. bonding between oil and clay surface. Chemical bonding interactions are also considered as the bases for the modeling approach presented in our chapter. A similar study by Mahani et al., (2015b) on carbonate rocks showed even slower reaction rates.

Evidence for the time-effect of wettability alteration was also found in the porescale study conducted by Bartels et al. (2017). The authors used a clay-functionalized micromodel system to investigate the LSE. A positive LSE for altering wettability was found for the crude oil, but this occurred slowly over several days, which showed that the alteration process may not be instantaneous. Additional evidence of the importance of reaction kinetics is observed during the aging process prior to coreflooding, where aging establishes an initial oil-wetness in the core by subjecting an oil saturated core sample to high-temperature pressure conditions. Aging is a time-consuming process which can take up to several days to establish the desired wettability state in a given core sample (Emery et al., 1970; Rivet et al., 2010). Thus, reaction kinetics can play an important role in the success of wettability alteration during LSWF. However, current models of LSWF are built under the assumption of equilibrium reaction conditions (Korrani and Jerauld, 2019; Qiao et al., 2015), even though experimental literature suggests otherwise.

In this research, we construct a unified mechanistic model of wettability alteration that can be adapted for both sandstone and carbonate reservoirs based on pseudocomponent identification of the wettability controlling species for both rock types. We present an example specific to carbonate rocks. We include the effects of reaction kinetics and dispersion that are incorporated through dimensionless groups, namely, Damköhler number and Pećlet number. We first present the underlying assumptions for the model development, followed by the governing equations. Next, we present the results of tuning and validation of the developed model against literature data. Finally, we discuss the results for known physical extremes of reaction kinetics and dispersion to capture their importance during LSWF.

6.2 Methodology

In this section, we define the main components of the model. First, we define the chemical reaction for wettability alteration. Next, we describe the procedure to lump pseudocomponents that are oil-wetting versus water-wetting based on the governing chemical mechanism of wettability alteration for both sandstones and carbonates. Lastly, we provide details about the model development, which is constructed in terms of component mass balances based on convective, dispersive, and reactive transport.

6.2.1. Defining the reaction for wettability alteration

The wettability alteration process involves numerous reactions that control the wetting state of the rock (Korrani and Jerauld, 2019; Qiao et al., 2016). Methods to reduce the number of reactions into lumped species are widely used in combustion and catalyst literature (Gao et al., 2016; Kuo and Wei, 1969). Combustion and catalytic systems involve complex networks of reactions that are in many cases impractical to measure and characterize. Therefore, for such systems, a reduced network of reactions is commonly used. In this chapter, we apply similar concepts by reducing the number of primary components and reactions to address the wettability alteration process during low-salinity waterflooding.

In the proposed model we assume that wettability alteration is essentially an adsorption/desorption process of the involved oil-wetting and water-wetting species, for

both sandstone and carbonate rocks. Therefore, we propose a binary component model to address wettability alteration. The use of a reduced number of components is advantageous because of reduced computational burden (Rasmussen et al., 2006). The model is based on the assumption that a binary model can accurately represent the real species involved in the process. The processes described for both sandstone and carbonate are modelled using proposed binary model illustrated in Fig 6. 1.

The two species in our model react with the rock surface kinetically. These two species compete to occupy the rock surface based on the equilibrium constant and species concentrations. The rock surface has a capacity (C_i) to hold a limited amount of either the oil-wetting or the water-wetting species. The oil-wetting species attached to the rock surface, *ow.s*, contributes to oil-wetness, whereas the attached water-wetting species, *ww.s*, contributes to water-wetness. For example, the initial wetting state (before brine injection) is determined by the equilibrium between the rock and wettability determining species available in the already-present formation brine. Upon the injection of a fresh brine, a change in the concentration of the wettability determining species is achieved. This causes the alteration in the wetting state of the rock.

The schematic shown in Fig 6. 2 illustrates the characteristic surface reaction during the wettability alteration for both sandstone and carbonate rocks, adapted from Lager et al., (2008) and Zhang et al., (2007), respectively. S1 shows polar oil components attached to the sandstone rock surface through the divalent cationic bridge at high (Ca^{2+}) salinity (oilwet state); S2 shows desorbed divalent cations from the surface during low (Ca^{2+}) salinity

(wettability alteration); and S3 shows monovalent cations attached to the surface (wettability altered: water-wet state). C1 shows negatively charged oleic acids attached to the positively charged carbonate rock surface (oil-wet state); C2 illustrates sulfate ions displacing oleic acids from the rock surface with the aid of calcium (wettability alteration); and C3 shows sulfate replacing oleic acids (wettability altered: water-wet state).

We use the following reversible Langmuir-type adsorption/desorption reaction to represent the wettability alteration process,

$$ow + ww.s \xleftarrow{k_f}{k_b} ww + ow.s$$
,

where, k_f is the forward reaction rate constant, k_b is the backward reaction rate constant , ow, ww are oil-wetting and water-wetting species concentrations in the water phase, ow.s, ww.s are oil-wetting and water-wetting species concentration on the rock surface.

The wettability alteration reaction is assumed to be reversible, where the rock wettability state is a function of the wettability determining species concentration. The method is not limited to only two components in the brine, but to two wettability determining species. We treat other components in the brine that do not participate significantly in the wettability alteration as "tracer" components in the water phase.



Fig 6. 1. Illustration of the proposed binary model surface reaction: ow, represents the oilwetting species in the water phase, ww represents the water-wetting species in the water phase, ow.s represents the oil-wetting species on the rock surface, and ww.s represents the water-wetting species on the rock surface.



Fig 6. 2 Wettability alteration mechanism in sandstones and carbonates, adapted from Lager et al., (2008) and Zhang et al., (2007), respectively.

We assume that the reaction occurs at the interface between the aqueous phase and the rock surface. The reaction rate is defined as a mass-based elemental reaction, where the rate is proportional to the mass concentrations as,

$$\frac{M_{ow}}{V_w t} = -k_f \frac{M_{ow}}{V_w} \frac{M_{ww.s}}{V_w} + k_b \frac{M_{ww}}{V_w} \frac{M_{ow.s}}{V_w} , \qquad (1)$$

where, the rate of consumption of the *ow* species is proportional to the concentrations of *ow* and *ww.s* species. Moreover, the rate of generation of the *ow* species is proportional to the concentrations of *ww* and *ow.s* species. We use the definition of equilibrium constant, $K = k_f / k_b$, so that the rate of reaction can be written as,

$$r_{ow} = -k_f \left(\rho_w \omega_{ow} \left(C_t - C_{ow,s} \right) \rho_{rock} \frac{\left(1 - \phi \right)}{\phi S_w} - \frac{1}{K} \rho_w \omega_{ww} C_{ow,s} \rho_{rock} \frac{\left(1 - \phi \right)}{\phi S_w} \right).$$
(2)

From reaction kinetics, we know that the rate of generation of the *ow* species is equal to the individual rates of generation of *ww.s* species, *ww* consumption, and *ow.s* consumption,

$$\frac{1}{r_{ow}} = \frac{1}{r_{ww,s}} = -\frac{1}{r_{ww}} = -\frac{1}{r_{ow,s}} \quad . \tag{3}$$

We incorporate this reaction model into reservoir simulation as described in section 6.2.3.

6.2.2. Lumping real chemical species into pseudocomponents

An important implementation step for the model is to determine chemical concentrations of the characteristic components to be used in the binary model. Lumping procedures are widely practiced in the petroleum industry, where the hydrocarbon phase consists of many components, which are computationally impractical to model individually. Instead, groups of components are lumped together and represented with equivalent thermodynamic properties for flash calculations (Pedersen and Christensen, 2006). Lumping is already being used in LSWF modeling where a variety of polar oleic components in the crude oil are represented by a single carboxylic acid that attaches to the rock surface (Qiao et al., 2016, 2015).

The ideal procedure for lumping components into pseudocomponents requires comprehensive laboratory studies. First, base composition should be defined, which normally will be the formation water composition. Then, the base composition of each component is altered systematically in the injection brine. Corefloods under controlled compositional variation can help assess individual component impact on wettability via oil recovery or contact angle measurement.

We lump components according to the surface charge of the rock surface as well as the ion-exchange mechanisms described in section 6.2.1 for wettability alteration. We hypothesize that species attach/detach to/from the rock surface based on charge affinity. For negatively charged sandstone, we lump divalent positively charged components such as calcium and magnesium ions which have the potential to form cationic bridging with the oleic acid as the oil-wetting species (Lager et al., 2008). Monovalent sodium ions, however, act as a water-wetting species (Khorsandi et al., 2017). For positively charged carbonate rocks, negatively charged oleic acids are defined the oil-wetting species, while negatively charged multivalent ions such as sulfate and bicarbonate ions are lumped as the water-wetting species (Qiao et al., 2015).

6.2.3. Overall mass balance for pseudocomponents

We construct a set of mass conservation equations for each component in each phase as (Lake et al., 2014),

$$-\frac{\partial}{\partial x}\left(u_{j}\rho_{j}\omega_{ij}-\varepsilon_{j}D_{ij}\frac{\partial(\rho_{j}\omega_{ij})}{\partial x}\right)+\varepsilon_{j}r_{ij}=\frac{\partial}{\partial t}\left(\omega_{ij}\rho_{j}\varepsilon_{j}\right) \qquad i=1...N_{c} \qquad j=1...N_{p} \quad .$$
(4)

Next, we construct a one-dimensional, isothermal, fully-implicit, compositional reservoir simulator for multiphase, multicomponent, convective-dispersive-reactive transport in porous media (see Appendix F). There are five principle unknowns for each discretized grid block: $P, S_w, \omega_{ow}, \omega_{ww}, C_{ow.s}$. To solve for the unknowns, we use five independent component mass balance equations (PDEs) for each grid block. We use one dispersion coefficient for all three aqueous components and two boundary conditions and one initial condition to solve for the principle unknowns.

The wettability state is determined by the fraction of the surface occupied by the oil-wetting species as defined by Qiao et al., (2015). That is,

$$\Psi_{i} = \Psi_{i \text{ water-wet}} \left(1 - \theta \right) + \Psi_{i \text{ oil-wet}} \theta \quad , \tag{5}$$

$$\theta = \frac{C_{ow.s}}{C_t} \quad , \tag{6}$$

where θ is the fraction of the reactive surface occupied by the oil-wetting species as a proxy for the wettability state, Ψ_i are the Brooks-Corey relative permeability parameters for both water-wet and oil-wet conditions, $S_{or,wirr}$, $k_{ro,rw}^o$, $n_{o,w}$ are oil and water residual phase saturations, end-point relative permeabilities, and Corey exponents, respectively.

Dimensionless analysis is helpful to determine the main contributing dimensional groups, using an analogy of the reservoir to a chemical engineering reactor (Fogler, 2006). We list the assumptions in the development of the governing equations in the Appendix F. The governing equation for *ow* species in the aqueous phase is,

$$-\frac{\partial}{\partial x}\left(u_{w}\omega_{ow}-\phi S_{w}D_{w}\frac{\partial(\omega_{ow})}{\partial x}\right)-k_{f}\rho_{rock}\left(1-\phi\right)\left[\omega_{ow}\left(C_{t}-C_{ow,s}\right)-\frac{1}{K}\omega_{ww}C_{ow,s}\right]=\frac{\partial}{\partial t}\left(\omega_{ow}\phi S_{w}\right).$$
(7)

Equation (7) is expressed in a dimensionless form (Eq. 10) using the following dimensionless groups:

$$u_{w} = Uu_{Dw}, \quad x = Lx_{D}, \quad t = \frac{\phi L}{U}t_{D}, \quad C_{i} = C_{i}C_{Di},$$
 (8)

$$Pe = \frac{UL}{\phi D_w} = \frac{\text{time for dispersion}}{\text{time for convection}}$$
(9)

$$Da = \frac{kC_{t}\rho_{rock}(1-\phi)L}{U} = \frac{\text{time for convection}}{\text{time for reaction}}$$
(10)

where, U is the total Darcy velocity of the phases, L is the length of the core/reservoir, Pe is the Peclet number, and Da is the Damköhler number. Thus, the dimensionless mass balance becomes,

$$-\frac{\partial}{\partial x_{D}}\left(u_{Dw}\omega_{ow}-S_{w}\frac{1}{Pe}\frac{\partial(\omega_{ow})}{\partial x_{D}}\right)-Da\left[\omega_{ow}\left(C_{Dt}-C_{Dow,s}\right)-\frac{1}{K}\omega_{ww}C_{Dow,s}\right]=\frac{\partial}{\partial t_{D}}\left(\omega_{ow}S_{w}\right).$$
(11)

Typical values of the parameters and the corresponding dimensionless groups at pore-scale and field-scale are shown in Table 6.1 and Table 6.2, respectively. Values for the Peclet number were found from the literature. The Peclet and Damköhler dimensionless groups vary significantly from the laboratory to field scale. Both the order of magnitude of the parameters, such as reaction rate constant, length scale, reservoir velocity, as well as the ratio of the variables as described by the dimensionless groups, are likely critical to recovery. To maintain consistency between field and laboratory scale, one should ensure that dimensionless numbers are similar at both scales.

Table 6. 1 Typical values of the parameters used for the estimation of Damköhler number (shown in Table 6.2) at the pore- and field-scale.

Parameter	Order of magnitude	Reference
Darcy velocity	$u = [0.03 \sim 2] \frac{m}{day}$	(Lake et al., 2014; Northrup et al., 1993)
Adsorption kinetics of calcium lignosulfate from porous media	$k = 2.5 \frac{g_{rock} / mg_{adsorbed}}{h}$	(Bai et al., 2009)
Rock capacity to hold the species (C_t)	0.4 mg/g	(Bai et al., 2009)
<i>Pore-scale:</i> Length scale of pore throat	~ 0.1 – 1 µm	(Nelson, 2009)
<i>Field-scale:</i> Length scale of the pseudo 1D reservoir	~ 1000 m	(Litvak and Angert, 2009)

Table 6. 2 Typical values of the different dimensionless groups at pore-scale and field-scale. The values shown for the Damköhler numbers are calculated from the parameters in Table 6.1.

Dimensionless group	Order of magnitude	Reference
Peclet number (Pe)	$\sim 10^{-2} - 10^{7}$	(Perkins and Johnston, 1963)
	~10 ⁻² - 10 ²	(Khrapitchev and Callaghan, 2003)
Damköhler number for second order reaction at pore-scale	$Da_{pore scale} = \frac{kC_t \rho_{rock} (1-\phi) L_{pore}}{u}$ ~ 1.4×10 ⁻¹	
Damköhler number for second order reaction at field-scale	$Da_{field \ scale} = \frac{kC_t \rho_{rock} (1-\phi) L_{field}}{u}$ ~ 1.4×10 ⁹	

6.3. Results and discussion

First, we validate the model by comparing simulation results to the limiting case given by the Buckley-Leverett (1942) solution. Second, we validate the dispersion model implemented in our simulator against the analytical single-phase convection-dispersion solution. Third, we validate the solution to the single-phase convection-dispersion-reaction equation. Fourth, we tune the proposed model and wettability mechanism with experimental data. Lastly, we examine the sensitivity of the model for limiting cases of dispersion and reaction kinetics.

6.3.1. Model validation

A comparison of the analytical Buckley-Leverett (1942) solution to the simulation results (discretized with 200 grid blocks) is shown in Fig 6. 3. The agreement is good for the 200 grid-block model, although there is slight spreading of the saturation front owing to numerical dispersion. The numerical solution approaches the analytical solution with the use of a finer grid, as it should.



Fig 6. 3 Comparison of water saturation profiles of numerical simulations performed with different grid-block sizes to the analytical Buckley-Leverett (1942) solution. Saturation profiles are shown as a function of dimensionless core sample length (X_D) at fixed pore volumes injected ($t_D = 0.2$).

Numerical dispersion is related to the grid-block size as estimated from the numerical Peclet number which is described as (Johns et al., 2002; Lantz, 1971),

$$Pe_{numerical} = \frac{2}{\Delta x_D} \tag{12}$$

The numerical Peclet number for simulations with 200 grid-blocks is 400, which represents relatively small numerical dispersion. Thus, for the cases presented in this chapter, numerical dispersion can be assumed to be much less than the physical dispersion added.

The proposed dispersion model is compared to the analytical single-phase convection-dispersion solution (Pe = 100) (Lake et al., 2014) in Fig 6. 4. Excellent agreement is also obtained.

Next, we validated our proposed reaction kinetics model. There is no analytical solution available specifically for the reaction that we have proposed in the methodology section. Thus, we compare our binary model solution to the semi-analytical solution developed in Mathematica (see Fig 6. 5), a software that is widely used in chemical engineering to solve single-phase convection-dispersion-reaction (CDR) problems (Kennedy and Carpenter, 2003).



 $\begin{array}{cccc} & ... & ... & 1 \\ & X_D \end{array}$ Fig 6. 4 Comparison of simulation to the analytical convection-dispersion solution at fixed t_D = 0.5 PVI (Pe = 100).



Fig 6. 5 Comparison of convection-dispersion-reaction (CDR) solutions via proposed binary model and semi-analytical solution for fixed $t_D = 0.5$ PVI (Pe = 100, Da = 100).

Fig 6. 5 shows close agreement for both solutions for the case of Pe = 100, Da = 100. The wettability alteration front ($x_D = 0.2$) moves slower than the injected fluid front ($x_D = 0.5$) even for single-phase reactive flow. The delay of the wettability front is caused by adsorption onto the rock surface for this single-phase conditions, similar to what is observed in the chemical engineering literature (Logan, 2012).

Next, we tune our proposed model to match experimental data. We used experimental data from (Fathi et al., 2010a) to validate the potential applicability of the proposed binary model (Fig 6. 6). These authors conducted core floods with carbonate rock, acidic crude oil, and brine with varying composition, such as formation water, seawater, and diluted seawater. The core flood data for fluid and reservoir properties, boundary/initial conditions, and tuned parameter values are given in Table 6. 3. We tuned relative permeability curves, *Da*, and *Pe*.

The carbonate rock used by (Fathi et al., 2010a) mainly consists of positively charged calcite mineral. Thus, we assume that the wettability determining species are negatively charged. As mentioned before, we combine the negatively charged sulfate and bicarbonate ions into the water-wetting pseudocomponent. Sulfate ions have an affinity to occupy the positively charged carbonate surface and displace the oleic acids (Austad et al., 2005; Fathi et al., 2010a; Strand et al., 2006). Moreover, we set the oil-wetting species to be a negatively charged dissociated oleic acid that partitions from the oil to the water phase, similar to the approach taken by (Qiao et al., 2015). The concentration of the dissociated

oleic acid is assumed to be constant in the reservoir. We assumed that the low concentration of acid is present in the water phase from the residual oil in the reservoir. Oleic acid is believed to be a crucial component for hydrocarbon adsorption on the rock surface (Purswani et al., 2017).

The coreflood experiment used three different brine compositions (formation, seawater, and diluted seawater). Here, we assumed no dispersion for the one-dimensional coreflood experiment ($Pe = \infty$). We tuned the relative permeabilities and reaction rates (Da) for the formation water and seawater waterfloods. These tuned parameters were used for predicting the oil recovery for diluted seawater waterflood. The model predicts no additional oil recovery with diluted seawater, same as shown in the experimental data.

There are many other cases where the injected brine composition may not result in improved oil recovery (Lager et al., 2008; Zhang and Morrow, 2006). It is likely that for those cases, the injected brine composition either does not contain wettability altering species, or that the reaction rate is very slow compared to the convection rate (Da < I).

Table 6. 3 Data used for simulation of experimental coreflood by (Fathi et al., 2010a)



Fig 6. 6 Wettability alteration simulation using the proposed binary model. Data is adopted from (Fathi et al., 2010a).

6.3.2. Wettability alteration under limiting physical conditions

In this section, we present wettability alteration cases for the limiting conditions of reaction kinetics and dispersion. The base case is a flood at residual oil saturation. The initial wetting state of the rock is 70% oil-wet, i.e. 70% of wettability determining surface is occupied by oil-wetting species. Other parameters used for setting up these simulations are provided in Table 6. 4. Spatial profiles of saturations, oil-wetness fraction, and water phase compositions at fixed injection condition ($t_D = 0.5 PVI$) are discussed for each limiting case.

Case 1: No wettability alteration reaction, no dispersion (Da = 0, $Pe = \infty$)

Fig 6. 7 shows that for the case of no wettability alteration and no dispersion, the wettability state is not affected by the convective or convective-dispersive flow. The salinity of the injected fluid will not affect wettability if there are no wettability altering species. For example, the experiments conducted by (Lager et al., 2008) with a reduced concentration of sodium ions in the injected brine, showed no improvement in oil recovery. This is likely because, in their experiments, sodium ions were not the major wettability-determining species and had little effect on the wetting state of the rock at the range of concentrations. Therefore, it is important to identify wettability determining species and tune associated concentration, instead of simply reducing salinity of the injected fluid.

Table 6. 4 Synthetic data used for simulation of cases for testing the effect of reaction kinetics and dispersion on wettability alteration under limiting physical conditions.

Reservoir and fluid properties	Initial/boundary conditions	End-point relative permeability parameters
$k = 2.96 \times 10^{-13} m^2 (= 300 md)$	initial conditions	$S_{or water-wet} = 0.05$
$\phi = 0.2$	$S_w(L,0) = 0.67$	$S_{wirr water-wet} = 0.25$
L = 0.3 m	$\omega_{spec1}(L,0) = 0.15$	$k_{rwwater-wet}^{o} = 0.3$
d = 0.0357 m	$\omega_{\text{spec}2}(L,0) = 0.05$	$k_{ro water-wet}^{o} = 0.9$
$\rho_w = 1000 kg / m^3$	$C_{\text{spec}}(L,0) = 0.007$	$n_{w water-wet} = 2$
$\mu_w = 10^{-3} Pa s$	spect.s (· ·)	$n_{o water-wet} = 2$
$\rho_o = 811.5 kg / m^3$	boundary conditions	$S_{or oil-wet} = 0.45$
$\mu_o = 2 \times 10^{-3} Pa s$	$q_{winj}(0,t) = 1.16 \times 10^{-11} m^3 / s \left(= 1 c m^3 / day\right)$	$S_{wirr oil-wet} = 0.25$
$\rho_{rock} = 2500 kg / m^3$	$\omega_{\text{snecl}}(0,t) = 0.01$	$k^o_{rw oil-wet} = 1$
$C_t = 0.01$	$\omega_{\rm max}(0,t) = 0.05$	$k^{o}_{ro\ oil-wet}=0.4$
	p(L,t) = 0.0 Pa	$n_{woil-wet} = 2$
	P(-,-) 0.02 0	$n_{o \ oil-wet} = 2$



Fig 6. 7 Spatial profiles for fixed $t_D = 0.5$ PVI: a. aqueous phase compositions, b. saturations, and c. rock oil-wetness fraction for no reaction and no dispersion case.

Case 2: Fast wettability alteration reaction, no dispersion ($Da = 10^5$, $Pe = \infty$)

Fig 6. 8 shows the results for the case of wettability alteration as a near instantaneous reaction, but with no dispersion. In this case, the ow species at the rock surface instantaneously reaches a new equilibrium state with the altered concentration of the injected fluid. However, the desorbed *ow* species now travels with the injected fluid. As the ow species desorbs into the water phase, its concentration in the injected fluid increases as it propagates further into the porous medium. Omekeh et al. (2012) suggested that dissolution and precipitation reactions change the injected fluid composition. This increased concentration of the ow species at the injected fluid front causes less desorption of the remaining ow.s species attached to the rock surface. For example, the injected fluid front is at $x_D = 0.75$ (Fig 6. 8a), whereas the wettability alteration front is at $x_D = 0.2$ (Fig 6. 8c). This suggests that the wettability alteration front moves slower than the injected fluid front, even though the wettability alteration reaction is instantaneous. A similar delay in wettability alteration was also shown by Khorsandi et al. (2017) using analytical solutions for two-phase flow. Brady and Krumhansl (2013) suggest that clays dissolve from sandstone to brine. Therefore, dissolution dampens the low salinity effect, and may cause the delay. This can have serious implications. For example, after injection of 1.0 PVI of the low-salinity brine, one may expect to have a water-wet reservoir, i.e. wettability alteration throughout the reservoir. However, only a small portion of the reservoir has actually been altered owing to the delay in the wettability alteration front. Thus, we would need to inject additional pore volumes of the low-salinity brine to achieve complete

wettability alteration throughout the reservoir, which may affect the project design and economics.



Fig 6. 8 Spatial profiles for fixed $t_D = 0.5$ PVI: a. aqueous phase compositions, b. saturations, and c. rock oil-wetness fraction for fast reaction and no dispersion case.

Case 3: Slow reaction (Da = 10), with and without dispersion (Pe = 10, \infty)

Fig 6. 9 shows the simulation results for a slow wettability alteration reaction with and without dispersion. It is observed that even with slow wettability alteration, the rock wettability is eventually altered successfully. However, the mobilized oil bank size is smaller than the oil bank formed with a fast reaction rate (Fig 6. 8). This confirms that for a slow reaction, the recovery will take a longer time. Moreover, to achieve the same final wettability state, one would need to inject larger slugs of low-salinity brine to counteract the slow alteration process. Larger slugs may be costly and can once again impact the project economically. For such reasons, including reaction kinetics during simulation of low-salinity waterflooding may impact economic decisions significantly.

Concentration gradients in the water phase spread due to dispersion (Fig 6. 9a). The concentration fronts spread more for the case with higher dispersion; however, there is no significant impact of dispersion (neither beneficial nor detrimental). The theoretical positive effect of dispersion is that the injected fluid composition will propagate further into the reservoir due to equilibration of the concentration gradient, thereby initiating the wettability alteration reaction sooner (Fig 6. 9c). However, formation brine would mix with injected water and spread the ion concentrations, thereby slowing down the reactions closer to the injection well (Fig 6. 9c). Al-Ibadi et al. (2019) suggest that salinity front proceeds faster when there is a dispersion in the system.



Fig 6. 9 Spatial profiles for fixed $t_D = 0.5$ PVI: a. aqueous phase compositions, b. saturations, and c. rock oil-wetness fraction for slow reaction (Da = 10) and no dispersion (Pe = ∞ , solid curves); with dispersion (Pe = 10, dashed curves) cases.

6.3.3. Effect of reaction kinetics and dispersion on oil recovery

In this section, we evaluate the impact on oil recovery based on our proposed model. We model the core floods reported in (Fathi et al., 2010a) and vary the effective reaction kinetics and dispersion level through the Damköhler and Peclet numbers, respectively.

Fig 6. 10 shows the effect of reaction kinetics on oil recovery under dispersion free conditions. A piston-like recovery of the oil bank is observed for the fast reaction, where the reaction rate is five orders of magnitude higher compared to the convection transport rate ($Da = 10^5$). Piston-like recovery gives the highest recovery because the recoverable oil bank forms instantaneously without a delayed response.

Fig 5.10 also shows that oil recovery is delayed when the reaction and convection rates are in similar order of magnitude (Da = 10). The slower reaction does not have piston-like recovery due to slow wettability alteration. That is, the oil bank is smeared for slow reaction (see Fig 6. 9b) compared to a fast reaction (see Fig 6. 8b). If the wettability reaction is slow in the field, but the reactions are assumed to be fast, then recovery from simulations will be overestimated.

More delayed oil recovery is observed for the case when the reaction rate is equal to the convection rate (Da = 1). This case may be observed in laboratory core floods, where the convection rate (reservoir velocity) is in the order of reaction rate (Mahani et al., 2015a). Particularly, core flood rates are typically at convection rates of one to four PV per

day, whereas the reaction rate is also in the order of days according to (Mahani et al., 2015a). Therefore, $Da \sim I$ is a reasonable estimate for core floods at the laboratory scale. The response of the system is delayed significantly. This delay could perhaps explain poor performance of some low salinity corefloods, where there is insufficient time for reactions to occur compared to the injection rate.

Fig 6. 11 demonstrates the effect of dispersion on oil recovery, where the ultimate recovery is delayed, even though the reaction rate is nearly instantaneous. Moreover, the piston-like recovery that is characteristic of fast reaction is smeared due to dispersion. The delay in recovery (compared to piston like recovery) is an important factor for project design and economics. Overall, even with significant dispersion (Pe = 10, Pe = 100), we observe that the ultimate recovery does not vary significantly for the fast wettability alteration reaction ($Da = 10^5$). For one-dimensional recovery, we have perfect sweep and the recovery is limited by the displacement efficiency only. For two- and three-dimensional simulations, where both sweep and displacement efficiencies can be affected by dispersion, the effects are likely to be significant.



Fig 6. 10 Effect of reaction kinetics on oil recovery with $Da = [1, 10, 10^5]$ and no dispersion (Pe = ∞).


Fig 6. 11 Effect of dispersion, $Pe = [10, 100, \infty]$, on oil recovery for a fast reaction $Da = 10^5$.

6.4. Chapter 6 conclusions

In this chapter, we developed a one-dimensional, multiphase, multicomponent, convection-diffusion-reaction model to estimate the effect of reaction kinetics and dispersion on the performance of low-salinity waterflooding (LSWF). The proposed binary model can represent complex brine composition, oleic phase composition, and rock surface composition. The model has the potential to address wettability alteration for different oil/rock/brine types, given that the wettability determining species are known. The following conclusions can be drawn within the scope outlined in this chapter.

- Slow reaction rates lead to slower wettability alteration, which delays incremental oil recovery because of a reduction in the amount of oil mobilized. To circumvent this situation, a larger slug size of the injected LSW may be used, subject to project economics.
- 2. The wettability alteration front is delayed behind the injected fluid front even in the limiting case of instantaneous wettability alteration reaction due to the desorption of excess salt from the rock surface.
- 3. Some laboratory core floods for LSWF may underestimate the recovery because the Damköhler number is not representative of field scale.
- 4. The effect of dispersion is less significant than that of reaction kinetics for the cases considered. Dispersion causes a delay in oil recovery; however, ultimate oil recovery remains less affected.

6.5 Chapter 6 nomenclature

Symbols	Description
CDR	Convection-dispersion-reaction
	Low-salinity effect
	Low-samily waternooding Cross sectional reservoir area (m^2)
A C	Dimensionless concentration of species i on the rock $i = aws$ www.
C_{Di}	Mass fraction of species i on rock surface $(k_a/k_{a-1})i = ows$, www.s
C_i	Rock adsorption capacity (k_{a} / k_{a})
d_{t}	Cross sectional reservoir diameter (m)
Da	Damköhler number
D_{ij}	Dispersion coefficient of species i in phase j (m^2/s)
k	Absolute permeability (m^2)
$k_{\scriptscriptstyle b}$	Backward reaction rate constant (s^{-1})
k_{f}	Forward reaction rate constant (s^{-1})
k_{rj}	Relative permeability of phase <i>j</i>
k^o_{ro}	End-point relative permeability to oil
k^o_{rw}	End-point relative permeability to water
Κ	Equilibrium constant
L	Reservoir length (<i>m</i>)
$M_{accumij}$	Mass accumulation of species i in phase j (kg)
M_{genij}	Mass generation of species i in phase j (kg)
M_{inij}	Mass in of species i in phase $j(kg)$
M_{outij}	Mass out of species i in phase j (kg)
$M_{_{OW}}$	Mass of oil-wetting species in water phase (kg)
$M_{ow.s}$	Mass of oil-wetting species on rock (kg)
$M_{_{WW}}$	Mass of water-wetting species in water phase (kg)
$M_{_{WW.S}}$	Mass of water-wetting species on rock (kg)
n _o	Corey exponent for end-point relative permeability to oil
n_w P.	Pressure of phase j (<i>Pa</i>)
J Po	Peclet number
q_{wini}	Injection rate of water phase (m^3/s)
r _{ij}	Rate generation of species <i>i</i> in phase $j (kg/m^3 s)$

r_{ow}	Rate generation of oil-wetting species $(kg/m^3 s)$
$r_{ow.s}$	Rate generation of oil-wetting species adsorbed on rock surface $(kg/m^3 s)$
r _{ww}	Rate generation of water-wetting species $(kg/m^3 s)$
$r_{_{WW.S}}$	Rate generation of water-wetting species adsorbed on rock surface $(kg/m^3 s)$
S _{or}	Residual oil saturation
S_w	Water saturation
S_{wirr}	Irreducible water saturation
t	Time (s)
t _D	Dimensionless time
<i>u</i> _j	Phase velocity (m/s)
u _{Dj}	Dimensionless velocity of phase <i>j</i>
U	Total velocity of all phases (m/s)
$V_{_{b}}$	Bulk volume (m^3)
V_{j}	Volume of phase $j(m^3)$
x	Distance (<i>m</i>)
<i>x</i> _{<i>D</i>}	Dimensionless distance
Greek symbols	
\mathcal{E}_{j}	Volume fraction of phase j in bulk volume
θ	Oil-wet fraction of the rock
$ ho_{j}$	Density of phase $j (kg/m^3)$
μ_{j}	Viscosity of phase j (Pa s)
ϕ	Porosity
Φ_{j}	Flow potential of phase j (Pa)
Ψ	Corey parameters for relative permeability for oil-wet and water-wet states
\mathcal{O}_{ij}	Mass fraction of species i in phase j
$\mathcal{O}_{_{ow}}$	Mass fraction of oil-wetting species in water phase
$arnothing_{\scriptscriptstyle WW}$	Mass fraction of water-wetting species in water phase

Chapter 7 Dissertation conclusions

This section presents a brief summary and main conclusions for each chapter.

CHAPTER 2

The second chapter focused on alkali-polymer phase behavior experiments and mechanisms. We analyzed real crude oil from Europe to identify favorable conditions to generate in-situ surfactants under various conditions, such as WOR, pH, and temperature. The important implications of this research are applicable for ultra-mature fields with acidic oil where in-situ surfactants generation may lead to additional oil recovery at low costs. Our findings indicate that soap generate maximum soap amount and an optimum phase behavior for low IFT. We explain how phase behavior becomes more complicated in the presence of asphaltenes/resins in crude oil and oil-soluble alcohols (see Fig 5.2).



Fig 2.24 Proposed mechanism of alcohol effect on the gel and stable emulsion formation in oleic phase.

Main conclusions:

- The improved oil recovery is evident via coreflood alkali injection experiments. The main cause of additional oil recovery is likely interfacial tension (IFT) reduction. The coreflood incremental recovery, in some cases, could be overestimated by the solubility of water in these macroemulsions within the oil phase.
- 2. We recommend sodium carbonate concentrations above 1g/l be used based on IFT measurements for the crude examined. Alcohol solubilizes polar oleic species and prevents the formation of the viscous phase. Alcohol concentrations to avoid the viscous layer at unity WOR is 4.4% by volume.
- 3. The phase behavior experiments do not undergo typical Winsor microemulsion behavior. Moreover, the experiments have shown more

complicated behavior, such as the formation of viscous upper macroemulsion phase and viscous layer at the oil-water interface.

- 4. Oil analysis showed the presence of various polar species instead of just carboxylic acids. The polar species under alkali environment likely form salt-crude complexes that potentially agglomerate into well-organized viscous networks at the oil-water interface. Moreover, the salt-crude complexes stabilize dispersed water droplets in oil and form viscous upper macroemulsion phase.
- 5. We proposed a reaction network that captures the salt-crude complex formation and explains viscous layer formation at the oil-water interface.
- 6. Coreflood results show great potential to use alkali based chemical slugs to improve the oil recovery, where the oil has acidic components.

The third chapter focuses on microemulsion phase behavior modelling with variable characteristic length. The improvement over previous constant characteristic length resolves thermodynamic inconsistency for phase behavior modeling. Moreover, the updated model can capture asymmetric phase behavior compared to existing models (See Fig. 3.12).



Fig 3. 12 Effect of variable characteristic length on two-phase lobes, $S^* = 1.0$ % wt.: a. constant length with S=1.05% wt. (HLD=0.1); b. constant characteristic length with S=0.905% wt. (HLD=-0.1); c. variable characteristic length with S=1.05% wt. (HLD=0.1); d. variable characteristic length with S=0.905 % wt. (HLD=-0.1).

The main conclusions are:

- Characteristic length varies inversely with most formulation variables as evidenced by experimental data. Salinity impacts characteristic length much less, however, than the other formulation variables.
- 2. The use of a variable characteristic length allows for asymmetric phase behavior modeling on either side of the optimum. This improvement can be very important, especially for three-phase regions that exist over a large change in HLD. Significantly improved fits to experimental data were demonstrated.
- 3. The asymmetry caused by a variable characteristic length affects the size of two-phase lobes as well. This occurs because the boundary of the threephase region is also the boundary of the two-phase lobes.

The fourth chapter focused on microemulsion phase behavior modelling improvements, such as thermodynamic constraints on multiphase regions, K-value implementation, and physical surfactant partition modelling (see Figure 4.9). This research was important to ensure a physical modelling of phase behavior that is further used for reliable physical predictions of the microemulsion properties.



Fig 4.9 Two-phase constraints: a. real ternary space; b. transformed ternary space. Black lines are two-phase constraints based on constant K-values and critical tie lines; pink triangle represents transformed space in a real ternary space. K-values constraints on two phase lobes are separated by 60 degrees in both pure and impure excess phases.

Main conclusions:

1. Two-phase lobes are constrained to exist within two limiting conditions: tie triangle

K-value and critical tie line boundary.

- 2. Two-phase lobes are constrained to be separated by at least 60 degrees in both real and transformed compositional spaces.
- 3. K-values are more suitable to model two-phase lobes, compared to using two-phase characteristic length. K-values show monotonic trends. K-values are physical compositional parameters that can be measured directly compared to hypothetical two-phase characteristic length that is inferred from the data.
- 4. Oil and water K-values remain invariant for real and transformed compositional spaces.

The fifth chapter focused on microemulsion phase viscosity modelling, particularly generation of so-called 'compositional viscosity map' (see Figure 5.1). The third chapter highlights the effect of surfactant on phase viscosity that is crucial when modelling the flow in porous media. The phase viscosity and interfacial tensions are both important parameters to consider when dealing with surfactants.



Fig 5.1 Generation of a viscosity map: a.) phase behavior near optimum conditions determined from a flash calculation; b.) viscosities for hypothetical single phase microemulsion compositions; c.) intersection of phase behavior with viscosities, phase splits eliminate viscosities; and d.) viscosity map variation at over optimum conditions, e.g. increased salinity.

The main conclusions are:

- The increase in viscosity with increasing surfactant concentration in pure oil and water can be explained by splitting and lumping surfactant volume into the oil and water domains, which is then modeled through Roscoe's (1952) suspension viscosity model.
- 2. A model for the percolation locus in compositional space is given to account for the observed increases in viscosity. We assume symmetry of the percolation locus owing to lack of viscosity data in the water continuous region.
- 3. The binary model by Khodaparast and Johns (2018) is successfully extended to ternary compositions.
- 4. The new compositional viscosity model fits experimental data well and predicts the viscosity in compositional space with acceptable accuracy ($R^2 > 0.75$).
- 5. Percolation exponent is shown to vary as a function of microemulsion oil composition. The variation is the result of micellar shape transitions in compositional space. A consistent trend is observed for average percolation exponent as a function of the oil composition.

The sixth chapter focused on studying the effects of dispersion and reaction kinetics on low salinity waterflooding. The reactive multicomponent/multiphase flow in porous media is modelled by combining reservoir simulator and reactive transport techniques. The effects are particularly important to consider when scaling from lab to field. For example, if the reaction takes four days to complete and the coreflood is conducted in one day, then observed oil recovery trends in the lab scale are not representative/transferable/scalable to the field scale application. The simulation results show a significant impact of reaction kinetics on the rate of wettability alteration compared to assuming instantaneous equilibrium (see Figure 6.8), whereas the dispersion does not affect the ultimate oil recovery.



Figure 6.8. Spatial saturation profiles for low salinity injection into mature oil field with S_{or} at high salinity, fixed time (0.5 PVI): a. fast reaction rate $Da=10^{11}$ results in sharp fronts, and clear oil bank that ensures piston like recovery; b. slow reaction rate Da=10 results in smeared fronts and smaller oil bank that corresponds to gradual recovery curve instead of piston-like displacement.

Main conclusions:

- Slow reaction rates lead to slower wettability alteration, which delays incremental oil recovery because of a reduction in the amount of oil mobilized. To circumvent this situation, a larger slug size of the injected LSW may be used, subject to project economics.
- 2. The wettability alteration front is delayed behind the injected fluid front even in the limiting case of instantaneous wettability alteration reaction due to the desorption of excess salt from the rock surface.
- 3. Some laboratory core floods for LSWF may underestimate the recovery because the Damköhler number is not representative of field scale.
- 4. The effect of dispersion is less significant than that of reaction kinetics for the cases considered. Dispersion causes a delay in oil recovery; however, ultimate oil recovery remains less affected.

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Appendices

Appendix A. Experimental procedure

We first removed asphaltene from the crude oil, where the asphaltene fraction is about 1% wt.. We dissolved the crude oil in n-pentane (alkane) and thoroughly mixed the mixture in a sonicator. Asphaltenes are large polar components in the crude and are insoluble in short alkanes, so when diluted with short alkanes asphaltene molecules agglomerate and precipitate in the mixture. The sample was left in a low-temperature environment for faster precipitation. After precipitation, the sample was centrifuged, so that precipitated asphaltenes accumulated to the bottom of the container. Next, asphaltenes were separated from the crude solution. Asphaltene free crude solution was then used for gas chromatography and mass spectrometry analysis. Total acid number experiment was conducted according to the procedure outlined by Fan and Buckley (2006).

We used double-distilled deionized water to ensure controlled conditions for the experiments: conductivity 1.07 μ S/cm, pH 5.65, non-detectable TDS, crude oil from OMV 16.TH reservoir without additives (further referred to as 'oil'). API of the oil was measured to be 25 API (0.903 g/cc) at room temperature. The viscosity of oil was found to be 59 cp at room temperature, 12 cp at 60 °C, and 8 cp at 90 °C. OMV alcohol (further referred to as 'alcohol') is used as delivered. The viscosity of alcohol is 22 cp at 60 °C, almost twice more viscous than the oil at the reservoir temperature. To ensure the constant composition

of both oil and alcohol, both containers were shaken before making the phase behavior experiments. Crude oil – alcohol – DI water was mixed at various compositions in ternary space to construct a ternary phase diagram.

For phase behavior scans, we prepared concentrated stock solutions of alkali and brine based on the weight percentage of chemicals and DI water. To perform scans of alkali and salinity, concentrated stocks were diluted with DI water. Weights were measured on electronic scales. Sodium chloride was used for salinity scans, and sodium carbonate for alkali scans (if not specified otherwise). Oleic and aqueous phases were mixed at the wateroil-ratio of unity (if not specified otherwise). The experiments were conducted in 5 ml sterile pipettes. The components were transferred into the pipettes with a repeater. The pipettes were then filled with argon and fire sealed. We mixed the fluids in the pipette and allowed sufficient time for equilibration of the interface. We mixed the fluids in the pipette using two techniques: single rigorous mixing and continuous rigorous mixing. Equilibration time varied for different samples. To evaluate equilibration time, we measured the interface height as a function of the inverse square root of time.

Single rigorous mixing was imposed in the pipettes after fire sealing, and the pipettes were left in a horizontal position to ensure a larger interface contact area for reactions to occur for half an hour, and then placed in a vertical position (unless mentioned otherwise). Continuous rigorous mixing involves repetitive single mixing every half an hour for 6-7 hours, and pipettes were left in a horizontal orientation.

Phase behavior tests were conducted using the following chemicals, supplies, and equipment:

- OMV crude oil from OMV 16.TH reservoir (without additives)
- Clariant cosolvent (further referred to as OMV alcohol)
- Sodium carbonate (by Sigma-Aldrich, assay >99.5%, 223530)
- Sodium chloride
- Sodium hydroxide (by Sigma-Aldrich, assay >98%, S8045)
- Hydrochloric acid (by Sigma-Aldrich, 37%, 320331)
- DI water (double distilled, conductivity 1.07 microS/cm, pH 5.65, TDS nondetectable)
- 5 ml glass serological pipet (by Fisherbrand)
- Mittler Toledo pH meter and supplies

Appendix B. Mixing procedure

The mixing procedure of oil-water-microemulsion systems was evaluated by two methods described earlier and illustrated in Fig. B1. Figure B1 shows that low alkali concentrations from 0.4% wt. to 1.2% wt. sodium chloride equilibrates to the same phase behavior. However, it is seen that concentrations above 1.6% wt. alkali have a different equilibrated state. Moreover, the viscous layer forms at the oil-water interface so that equilibration is not likely to occur quickly (and therefore, the systems are not in equilibrium).




Figure B1. Equilibrated phase behavior for alkali scan for a. single rigorous mixing; and b. continuous rigorous mixing.

The viscous layer likely causes the different equilibration states. The oil acids partition into the aqueous phase through the interface to undergo further reactions. However, if the viscous interface is formed, the reaction is essentially stopped because species cannot transfer between phases through the viscous layer. When single rigorous mixing is imposed, the reactions stop sooner when the first viscous layer forms and the final equilibrium state is not reached. Moreover, when continuous rigorous mixing is imposed we break the viscous layer and a new interface becomes available for the reactions to occur. Therefore, two mixing procedures correspond to two different extents of the reaction, which leads to different equilibration states.



Figure B2. Phase equilibration with time for a. 1.2% wt. alkali; b. 2.8% wt. alkali.

At low alkali concentration (Fig. B2a) the equilibrated phases approach each other implying true equilibrium, whereas higher alkali concentrations (>1.6% wt.) do not represent true equilibrium, but rather extremely slow equilibration due to the formation of the viscous layer at the water-oil interface.

Appendix C. Crude oil sensitivity to electric field



Figure C1. Demonstration of polar nature of the crude oil.

In the experiments above on Fig. C1, the glass beaker is rubbed with paper where a static electric field is generated due to a net surface charge between the glass surface and pipette. Oil is injected into the beaker using a pipette. Under normal conditions, nonpolar crude would drip into the beaker vertically, and the static electric field would not affect the process. However, under the influence of an electric field, the crude oil flows more horizontally as a thin stream towards the glass surface, instead of by drops downward. This may occur owing to an abundance of polar components in the crude, which stream under the static electric field. As more and more oil droplets reach the charged surface of the glass, the electric field is neutralized. When the field is neutralized, the crude starts dripping in drops vertically instead of forming a thin stream. The phenomenon is referred to as a 'Taylor cone' (Konermann et al., 2012). This observation validates the abundant presence of polar components in crude oil.

Appendix D. HLD coefficient for salinity

This section discusses how I-ratio takes $c_1=(dHLD/dlnS)$ coefficient into account. We use the following HLD definition

$$\mathcal{H} = c_0 \ln K_s^{ow}$$

If we only consider salinity as formulation variables, we can express change in HLD as:

$$d\mathcal{H} = d\left(c_0 \ln K_s^{ow}\right) = \left(\frac{\partial \mathcal{H}}{\partial \ln S}\right) d\ln S$$

We assume partial coefficient to be constant:

$$\mathcal{H} - \mathcal{H}_{ref} = c_0 \ln \left(\frac{K_s^{ow}}{K_s^{ow}_{ref}} \right) = c_1 \ln \frac{S}{S_{ref}}$$

We take reference state at any optimum to get:

$$\mathcal{H} = c_0 \ln \left(\frac{K_s^{ow}}{K_s^{ow}} \right) = c_1 \ln \frac{S}{S^*}$$

Salager group suggests that $c_1 = 1$. For a salinity scan the I-ratio will adjust to a nonphysical value if the value of c_1 is not set to approximately one. In fact, any value of c_1 would be applicable to use HLD-NAC model, because c_1 contribution is taken care of in the I-ratio.

However, we would lose the physical implications of the parameters, such as expected range of I-ratio to be between zero and one. Type III HLD-NAC equations are as follows:

$$\frac{1}{\sigma_o} - \frac{1}{\sigma_w} = -3I\mathcal{H}$$
 and $\frac{1}{\sigma_o} + \frac{1}{\sigma_w} = \frac{6I}{\xi_D^{\max}}$

We use the above HLD expression in HLD-NAC model:

$$\frac{1}{\sigma_o} - \frac{1}{\sigma_w} = -3Ic_1 \ln \frac{S}{S^*}$$

For average curvature equation we multiply and divide RHS with c_1 :

$$\frac{1}{\sigma_o} + \frac{1}{\sigma_w} = \frac{6Ic_1}{\xi_D^{\max}c_1}$$

We now can assign $\mathcal{H}_{new} = \ln \frac{S}{S^*}$, $I_{new} = Ic_1$ and $\xi_D^{\max} = \xi_D^{\max} c_1$, so we get:

$$\frac{1}{\sigma_o} - \frac{1}{\sigma_w} = -3I_{new}\mathcal{H}_{new} \text{ and } \frac{1}{\sigma_o} + \frac{1}{\sigma_w} = \frac{6I_{new}}{\xi_D^{max}}$$

Thus, we get same HLD-NAC equations where c_1 is incorporated into l and ξ_D^{\max} . Below we show an example where phase behavior can be modelled identically using different c_1 coefficients: Same procedure works for any HLD coefficient K, α , β . Any

uncertainty related to HLD coefficients is taken care of in the I-ratio.



Figure D1. Experimental data from Roshanfekr (2010) for octane. Salinity scan in range 2.79 to 3.8 wt%. models with $c_1 = 1$ and $c_1 = 5$ yield into identical results when I and ξ_D^{max} are adjusted.



Figure D2. a. model parameters I = 0.25, $c_1 = 1$, $\xi_D^{max} = 5.625$, as a result HLD spans -0.15 to 0.15; b. model parameters I = 0.05, $c_1 = 5$, $\xi_D^{max} = 1.1250$, as a result HLD spans -0.7 to 0.7; c. model parameters I = 0.025, $c_1 = 10$, $\xi_D^{max} = 0.5625$, as a result HLD spans -1.5 to 1.5. Data from Roshanfekr (2010).

Appendix E. Minimum bound on the value of percolation exponent κ

Percolation critical exponent κ is an exponent parameter in percolation theory where clusters agglomerate into a continuous network (Stauffer, 1979, Rubenstein and Colby, 2003). By definition, the continuous fraction of domain *i* must be less than or equal to (equal only at domain inversion) the overall composition as shown:

$$C_{ic} = C_{DI} \left(\frac{C_i - C_i^{cr}}{C_{DI} - C_i^{cr}} \right)^{\kappa_i} < C_i,$$

Thus,

$$\kappa_i \ln \left(\frac{C_i - C_i^{cr}}{C_{DI} - C_i^{cr}} \right) < \ln \left(\frac{C_i}{C_{DI}} \right).$$

Because $\ln\left(\frac{C_i - C_i^{cr}}{C_{DI} - C_i^{cr}}\right) < 0$:

$$\kappa_i > \frac{\ln\left(\frac{C_i}{C_{DI}}\right)}{\ln\left(\frac{C_i - C_i^{cr}}{C_{DI} - C_i^{cr}}\right)}.$$

Simple arithmetic shows that for a, b and c positive:

$$\frac{a}{b} > \frac{a-c}{b-c} \; .$$

These ratios are less than unity, which means:

$$\left|\ln\left(\frac{a}{b}\right)\right| < \left|\ln\left(\frac{a-c}{b-c}\right)\right|.$$

Thus,

$$0 < \frac{\ln\left(\frac{C_i}{C_{DI}}\right)}{\ln\left(\frac{C_i - C_i^{cr}}{C_{DI} - C_i^{cr}}\right)} < 1.$$

The ratio in the above inequality depends on C_i , C_{DI} , and C_i^{cr} . However, in the limiting case of $C_i \rightarrow C_{DI}$, L'Hopital's rule gives:

$$\lim_{C_{i} \to C_{DI}} \frac{\ln\left(\frac{C_{i}}{C_{DI}}\right)}{\ln\left(\frac{C_{i} - C_{i}^{cr}}{C_{DI} - C_{i}^{cr}}\right)} = \lim_{C_{i} \to C_{DI}} \frac{\frac{1}{C_{DI}}\left(\frac{1}{\frac{C_{i}}{C_{DI}}}\right)}{\frac{1}{C_{DI} - C_{i}^{cr}}\left(\frac{1}{\frac{C_{i} - C_{i}^{cr}}{C_{DI} - C_{i}^{cr}}}\right)} = \lim_{C_{i} \to C_{DI}} \frac{C_{i} - C_{i}^{cr}}{C_{i}} = 1 - \frac{C_{i}^{cr}}{C_{DI}},$$

which for the current assumption of $C_{DI} = 0.5$ in our model yields,

$$\lim_{C_i \to C_{DI}} \kappa_i > \lim_{C_i \to C_{DI}} \frac{\ln\left(\frac{C_i}{C_{DI}}\right)}{\ln\left(\frac{C_i - C_i^{cr}}{C_{DI} - C_i^{cr}}\right)} = 1 - 2C_i^{cr} \cdot \frac{1}{2C_i^{cr}}$$

In the other limit of $C_i \rightarrow C_i^{cr}$, we could readily show that:

 $\lim_{C_i\to C_i^{cr}}\kappa_i>0.$

Therefore, the more restrictive bound should be satisfied. Thus, as $C_o \to 1$, $C_w^{cr} \to 0$, , so $\kappa_w > 1$. Similarly, as $C_w \to 1$, $C_o^{cr} \to 0$, therefore $\kappa_o > 1$.

Appendix F. Reservoir simulation with kinetics and dispersion

We consider an arbitrary volume in a Cartesian space:



$$M_{in} - M_{out} + M_{gen} = M_{accum} .$$
 (1)

Further, we consider a 1D case with convective and dispersive flow of component i within the phase j as follows:

$$M_{in/out \ ij} = A \left(u_j \rho_j \omega_{ij} - \varepsilon_j D_{ij} \frac{\partial (\rho_j \omega_{ij})}{\partial x} \right) \Delta t \qquad (2)$$

For the generation term, we consider a source term (well) and a reaction generation/consumption term as follows:

$$M_{genij} = \left(q_j \rho_j \omega_{ij} + V_j r_{ij} \varepsilon_j\right) \Delta t \quad .$$
(3)

The accumulation term is:

$$M_{accum \ ij} = V_b \left(\left(\omega_{ij} \rho_j \varepsilon_j \right) |_{t+\Delta t} - \left(\omega_{ij} \rho_j \varepsilon_j \right) |_t \right) . \tag{4}$$

Thus, the mass balance for a species in the arbitrary volume is:

$$A\left(u_{j}\rho_{j}\omega_{ij}-\varepsilon_{j}D_{ij}\frac{\partial(\rho_{j}\omega_{ij})}{\partial x}\right)\Delta t\bigg|_{in}-A\left(u_{j}\rho_{j}\omega_{ij}-\varepsilon_{j}D_{ij}\frac{\partial(\rho_{j}\omega_{ij})}{\partial x}\right)\Delta t\bigg|_{out}+q_{j}\rho_{j}\omega_{ij}\Delta t+V_{b}r_{ij}\varepsilon_{j}\Delta t=V_{b}\left(\left(\omega_{ij}\rho_{j}\varepsilon_{j}\right)|_{t+\Delta t}-\left(\omega_{ij}\rho_{j}\varepsilon_{j}\right)|_{t}\right)$$
(5)

Now we divide the entire equation by $V_b = A\Delta x$ and Δt

$$\frac{\left(u_{j}\rho_{j}\omega_{ij}-\varepsilon_{j}D_{ij}\frac{\partial(\rho_{j}\omega_{ij})}{\partial x}\right)_{in}-\left(u_{j}\rho_{j}\omega_{ij}-\varepsilon_{j}D_{ij}\frac{\partial(\rho_{j}\omega_{ij})}{\partial x}\right)_{out}}{\Delta x} + \frac{q_{j}\rho_{j}\omega_{ij}}{V_{b}}+\varepsilon_{j}r_{ij}=\frac{\left(\omega_{ij}\rho_{j}\varepsilon_{j}\right)_{l_{t+\Delta t}}-\left(\omega_{ij}\rho_{j}\varepsilon_{j}\right)_{l_{t}}}{\Delta t},$$
(6)

allowing $\Delta x, \Delta t \rightarrow 0$,

$$-\frac{\partial}{\partial x}\left(u_{j}\rho_{j}\omega_{ij}-\varepsilon_{j}D_{ij}\frac{\partial(\rho_{j}\omega_{ij})}{\partial x}\right)+\frac{q_{j}\rho_{j}\omega_{ij}}{V_{b}}+\varepsilon_{j}r_{ij}=\frac{\partial}{\partial t}\left(\omega_{ij}\rho_{j}\varepsilon_{j}\right) \qquad i=1...N_{c} \qquad j=1...N_{p} \quad .$$
(7)

Table A1outlines the assumptions made in our model.

Assumption	Implication	Remarks
Two mobile phases exist: w-water, o -oil	Convention and dispersion transport happen at oleic and aqueous phases $j = o, w$	Treatment of adsorbed species on a solid phase will be shown in the later sections
6 components exist: 0, W, OW, WW, OW.S, WW.S	Mass balance is written for each component, $i = o, w, ow, ww, ow.s, ww.s$	
Convective transport is modeled using Darcy's law	$u_j = -\frac{k_{ij}k}{\mu_j} \frac{\partial \Phi_j}{\partial x}$	
Gravitational effects are negligible	$\Phi_j = P_j$	
Capillary pressure is negligible	$P_o = P_w$	Wettability of the rock surface affects capillary- saturation curve,

Table A1. Model assumptions

		however here we assume that capillary effects are negligible for forced displacement
Oleic phase consists of only hydrocarbon components	$\omega_{oo} = 1$	
No reactions in oleic phase	$r_{oo} = 0$	
Rock surface may have two states: oil-wet and water-wet	$C_t = C_{ow.s} + C_{ww.s}$	$C_{ow.s}$ is an oil-wet state, $C_{ww.s}$ is a water-wet state
Water phase consists of water, ow, ww	$\omega_{w} + \omega_{ow} + \omega_{ww} = 1$	
Dispersion of components is characterized through a constant dispersion coefficient	$D_{ij} = D_j$ $D_w = D_{oww} = D_{www} = D_{ww}$	The oleic phase has only an oil component, therefore no dispersion can occur within the oleic phase
Homogeneous reservoir	k = const	
Incompressible fluid and rock	$\rho_j = const, \phi = const$	
Constant viscosity fluids	$\mu_j = const$	

Thus upon applying these assumptions, the phase equations summed over each species gives following compositional equation set:

$$-\frac{\partial}{\partial x}\left(u_{j}\rho_{j}\omega_{ij}-\varepsilon_{j}D_{ij}\frac{\partial(\rho_{j}\omega_{ij})}{\partial x}\right)+\frac{q_{j}\rho_{j}\omega_{ij}}{V_{b}}+\varepsilon_{j}r_{ij}=\frac{\partial}{\partial t}\left(\omega_{ij}\rho_{j}\varepsilon_{j}\right),$$
(8)

hydrocarbon:

$$-\frac{\partial}{\partial x} \left(-\frac{k_{ro}k}{\mu_o} \frac{\partial P}{\partial x} \rho_o \right) + \frac{q_o \rho_o}{V_b} = \frac{\partial}{\partial t} \left(\rho_o \phi S_o \right)$$
(9)

water:

$$-\frac{\partial}{\partial x}\left(-\frac{k_{rw}k}{\mu_{w}}\frac{\partial P}{\partial x}\rho_{w}\left(1-\omega_{ow}-\omega_{ww}\right)-\phi S_{w}D_{w}\frac{\partial\left(\rho_{w}\left(1-\omega_{ow}-\omega_{ww}\right)\right)}{\partial x}\right)+\frac{q_{w}\rho_{w}\left(1-\omega_{ow}-\omega_{ww}\right)}{V_{b}}=\frac{\partial}{\partial t}\left(\left(1-\omega_{ow}-\omega_{ww}\right)\rho_{w}\phi S_{w}\right)$$
,(10)

ow:

$$-\frac{\partial}{\partial x}\left(-\frac{k_{rw}k}{\mu_{w}}\frac{\partial P}{\partial x}\rho_{w}\omega_{ow}-\phi S_{w}D_{w}\frac{\partial(\rho_{w}\omega_{ow})}{\partial x}\right)+\frac{q_{w}\rho_{w}\omega_{ow}}{V_{b}}+\phi S_{w}r_{ow}=\frac{\partial}{\partial t}\left(\omega_{ow}\rho_{w}\phi S_{w}\right)$$
(11)

ww:

$$-\frac{\partial}{\partial x}\left(-\frac{k_{rw}k}{\mu_{w}}\frac{\partial P}{\partial x}\rho_{w}\omega_{ww}-\phi S_{w}D_{w}\frac{\partial(\rho_{w}\omega_{ww})}{\partial x}\right)+\frac{q_{w}\rho_{w}\omega_{ww}}{V_{b}}+\phi S_{w}r_{ww}=\frac{\partial}{\partial t}\left(\omega_{ww}\rho_{w}\phi S_{w}\right)$$
(12)

ow.s:

$$\phi S_{w} r_{ow.s} = \frac{\partial}{\partial t} \left(C_{ow.s} \rho_{rock} \left(1 - \phi \right) \right) \,. \tag{13}$$

We now implement a finite difference approximation on mass balance PDE (central difference in space, forward difference in time, fully implicit scheme):

hydrocarbon:

$$\rho_{o} \frac{k}{\mu_{o} \Delta x^{2}} \left[k_{ro\ i+1/2}^{n+1} \left(P_{i+1/2}^{n+1} - P_{i}^{n+1} \right) - k_{ro\ i-1/2}^{n+1} \left(P_{i}^{n+1} - P_{i-1/2}^{n+1} \right) \right] + \frac{q_{o\ i}^{n+1}}{V_{b}} \frac{\rho_{o}}{\Delta t} \left(S_{w\ i}^{n} - S_{w\ i}^{n+1} \right)$$
(14)

water:

$$\rho_{w} \frac{k}{\mu_{w} \Delta x^{2}} \Big[k_{rw}^{n+1} \Big(P_{i+1/2}^{n+1} - P_{i}^{n+1} \Big) \Big(1 - \omega_{ow}^{n+1} - \omega_{ow}^{n+1} \Big) - k_{rw}^{n+1} \Big(P_{i}^{n+1} - P_{i-1/2}^{n+1} \Big) \Big(1 - \omega_{ow}^{n+1} - \omega_{ow}^{n+1} \Big) \Big] + \frac{\phi D_{w} \rho_{w}}{\Delta x^{2}} \Big[S_{w}^{n+1} \Big(-\omega_{ow}^{n+1} - \omega_{ww}^{n+1} + \omega_{ow}^{n+1} + \omega_{ow}^{n+1} \Big) - S_{w}^{n+1} \Big(-\omega_{ow}^{n+1} - \omega_{ow}^{n+1} + \omega_{ow}^{n+1} + \omega_{ow}^{n+1} \Big) \Big] + \frac{q_{w}^{n+1} \rho_{w} \Big(1 - \omega_{ow}^{n+1} - \omega_{ww}^{n+1} \Big)}{V_{b}} = \frac{\rho_{w} \phi}{\Delta t} \Big(\Big(1 - \omega_{ow}^{n+1} - \omega_{ww}^{n+1} \Big) S_{w}^{n+1} - \Big(1 - \omega_{ow}^{n} - \omega_{ww}^{n} \Big) S_{w}^{n} \Big)$$
(15)

ow:

$$\rho_{w} \frac{k}{\mu_{w} \Delta x^{2}} \Big[k_{rw \, i+1/2}^{n+1} \Big(P_{i+1/2}^{n+1} - P_{i}^{n+1} \Big) \omega_{ow \, i+1/2}^{n+1} - k_{rw \, i-1/2}^{n+1} \Big(P_{i}^{n+1} - P_{i-1/2}^{n+1} \Big) \omega_{ow \, i-1/2}^{n+1} \Big] + \\
+ \frac{\phi D_{w} \rho_{w}}{\Delta x^{2}} \Big[S_{w \, i+1/2}^{n+1} \Big(\omega_{ow \, i+1}^{n+1} - \omega_{ow \, i}^{n+1} \Big) - S_{w \, i-1/2}^{n+1} \Big(\omega_{ow \, i}^{n+1} - \omega_{ow \, i-1}^{n+1} \Big) \Big] + \\
+ \rho_{rock} \Big(1 - \phi \Big) \rho_{w} \Big[-k \Big(\omega_{ow \, i}^{n+1} \Big(C_{t} - C_{ow.s \, i}^{n+1} \Big) - \frac{1}{K} \omega_{ww \, i}^{n+1} C_{ow.s \, i}^{n+1} \Big) \Big] + \\
+ \frac{q_{w \, i}^{n+1} \rho_{w} \omega_{ow \, i}^{n+1}}{V_{b}} = \frac{\rho_{w} \phi}{\Delta t} \Big(\omega_{ow \, i}^{n+1} S_{w \, i}^{n+1} - \omega_{ow \, i}^{n} S_{w \, i}^{n} \Big)$$
(16)

ww:

$$\begin{split} \rho_{w} \frac{k}{\mu_{w} \Delta x^{2}} \Big[k_{rw \, i+1/2}^{n+1} \left(P_{i+1/2}^{n+1} - P_{i}^{n+1} \right) \omega_{ww \, i+1/2}^{n+1} - k_{rw \, i-1/2}^{n+1} \left(P_{i}^{n+1} - P_{i-1/2}^{n+1} \right) \omega_{ww \, i-1/2}^{n+1} \Big] + \\ &+ \frac{\phi D_{w} \rho_{w}}{\Delta x^{2}} \Big[S_{w \, i+1/2}^{n+1} \left(\omega_{ww \, i+1}^{n+1} - \omega_{ww \, i}^{n+1} \right) - S_{w \, i-1/2}^{n+1} \left(\omega_{ww \, i}^{n+1} - \omega_{ww \, i-1}^{n+1} \right) \Big] + \\ &+ \rho_{rock} \left(1 - \phi \right) \rho_{w} \Big[k \Big(\omega_{ow \, i}^{n+1} \Big(C_{t} - C_{ow \, s \, i}^{n+1} \Big) - \frac{1}{K} \omega_{ww \, i}^{n+1} C_{ow \, s \, i}^{n+1} \Big) \Big] + \\ &+ \frac{q_{w \, i}^{n+1} \rho_{w} \omega_{ww \, i}^{n+1}}{V_{b}} = \frac{\rho_{w} \phi}{\Delta t} \Big(\omega_{ww \, i}^{n+1} S_{w \, i}^{n+1} - \omega_{ww \, i}^{n} S_{w \, i}^{n} \Big) \end{split}$$

(17)

ow.s:

$$\rho_{rock} (1-\phi) \rho_{w} \left[k \left(\omega_{ow\,i}^{n+1} \left(C_{t} - C_{ow,s\,i}^{n+1} \right) - \frac{1}{K} \omega_{ww\,i}^{n+1} C_{ow,s\,i}^{n+1} \right) \right] + \\ = \frac{\rho_{rock} (1-\phi)}{\Delta t} \left(C_{ow,s\,i}^{n+1} - C_{ow,s\,i}^{n} \right)$$
(18)

The species attached to the rock surface do not undergo convective and dispersive transport. The only means of surface concentration alteration is reaction. Thus, when species are released from the rock surface to the aqueous phase, the species are transported with/within the aqueous phase.

We implement a numerical Newton Raphson protocol to solve the system of equations. The proposed binary simulator model is implemented using MATLAB ® R2018a software.

VITA

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Daulet Magzymov was born in the year of 1992 in Ekibastuz, Kazakhstan. He graduated from Pavlodar Kazakh Turkish High School with highest honors Golden Medal 'Altyn Belgi' in 2010. After graduation, Daulet enrolled in newly founded world-class academic institution Nazarbayev University in Astana, Kazakhstan. There he earned Bachelor of Engineering degree in Chemical Engineering with Honors in 2015. Daulet then came to State College, PA to pursue his PhD degree in Energy and Mineral Engineering (Petroleum and Natural Gas Engineering option), The Pennsylvania State University. He defended his doctoral dissertation in 2020.