

# Formulations for chemical enhanced oil recovery biology essay

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The research presented in this work is to place high public presentation surfactant preparations for chemical enhanced oil recovery of a rough oil from a Kansas reservoir and provides counsel for its future field application. Phase behavior experiments are conducted to choose optimum surfactant preparation and nucleus inundations are conducted to formalize their oil recovery efficiency. This research focuses on stage behaviour design methodological analysis and nucleus inundation design scheme. In this chapter, research motive and reason are discussed in following subdivisions.

## **Research Motivation**

Presently, waterflood as a conventional oil recovery means leaves more than half of the original oil in sandstone reservoirs, and even more in carbonate reservoirs. In order to retrieve the residuary oil, interfacial tenseness demands to be reduced well to increase the capillary figure to approximately ten thousand fold the capillary figure of waterflood. Wetting agents could solubilize H<sub>2</sub>O and oil in a microemulsion stage, which could cut down interfacial tenseness between microemulsion and water/oil to ultralow.

Other chemicals such as co-surfactant, co-solvent, alkali, and electrolyte are normally blended with primary wetting agent to bring forth clear, fluid, and stable surfactant preparation that has the highest solubilization ratio of water/oil, i. e. the lowest interfacial tenseness. In order to choose the best surfactant preparation, a three phase method, developed by Levitt ( 2006 ) , Jackson ( 2006 ) and Flaaten ( 2007 ) at the University of Texas at Austin, are adopted in my research. The first phase selects a list of wetting agents based upon informations and cognition of surfactant construction and the

mark reservoir and rough oil belongings. The 2nd phase screens the surfactant preparation with rough oil in stage behaviour experiments, which evaluates phase behavior public presentation through solubilization ratio ( which is reciprocally relative to interfacial tenseness ) , microemulsion viscousness, equilibration clip, aqueous stage stableness bound and optimum salt among other features.

The 3rd phase tests the optimum surfactant preparation in research lab nucleus inundation experiments.

## **Research Rationality**

This research evaluates a rough oil in a limestone reservoir located in western Kansas. The reservoir has been H<sub>2</sub>O flooded for the last 15 old ages and presently is at a phase of H<sub>2</sub>O inundation with low oil cut. The formation seawater is high salt seawater with moderate hardness. In order to choose the right wetting agent preparation, some commercially available and promising wetting agents are selected based on surveies of Levitt ( 2006 ) , Jackson ( 2006 ) and Flaaten ( 2007 ) and tested with the petroleum oil foremost ; so they are compared to and optimized with some other freshly developed wetting agents from other companies.

After optimum surfactant preparation passes all standards, nucleus inundations are so conducted to formalize the oil recovery efficiency. In order to understand the chemical inundation procedure good, soft seawater with tantamount salt to surfactant slug alternatively of high salt difficult formation seawater is used to saturate and waterflood the nucleus in the initial nucleus inundation experiments. Besides, because chemical implosion

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therapy in sandstone nucleus is much more extensively studied than in limestone, sandstone is used for nucleus implosion therapy at first. After nucleus inundations in sandstone validate the high oil recovery efficiency of the surfactant preparation, formation seawater and limestone are so used in subsequent experiments to measure preparation public presentation near to existent reservoir conditions.

## **Summary of Chapters**

Chapter 2 discusses background and literature information, chemical constituent construction and rules of chemical mixture and nucleus inundation design for EOR applications. Chapter 3 provides an experimental description of the stage behaviour and nucleus inundation experiments, and describes the equipment, methodological analysis and information computations used in the research. Chapter 4 summarizes stage behaviour testing consequences and the optimum preparation design procedure. Chapter 5 nowadays consequences of different nucleus inundation designs for a rough oil and analysis of nucleus inundation force per unit area informations and wastewater belongings. Chapter 6 nowadays a drumhead and decision of all experimental consequences and proposes future work and way for farther research.

## **Chapter 2: Literature Reappraisal**

### **Introduction**

This chapter provides background and a literature reappraisal on the theory and methodological analysis used in this research. It describes phase behaviour testing experiments, including microemulsion word picture and its

mechanism to mobilise oil, and the functions and effects of chemicals in stage behaviour experiments.

It so reviews the basic rules of nucleus inundation design and introduces the petroleum oil evaluated in this research.

## **Phase Behavior Screening**

### **Micro-emulsion**

#### **Micro-emulsion Word picture**

Bourrel and Schechltter ( 1988 ) define microemulsion stage as a thermodynamically stable stage under certain conditions and in theory it ne'er separates into two stages unless conditions change. Microemulsion is different from " macroemulsion " , which is thermodynamically unstable even though it may be kinetically stable. However, before Bourrel and Schechltter defined microemulsion, Winsor ( 1954 ) described the stage behaviour for the mixture of an oil/water/surfactant system. He identified the three types of stage equilibria in microemulsion stage behaviour as Type I, Type II and Type III.

Type I microemulsion is an oil in H<sub>2</sub>O microemulsion with extra seawater stage, besides referred as Type II ( - ) because the stage diagram has a negative incline. Type II microemulsion is H<sub>2</sub>O in oil microemulsion with extra oil stage, besides referred as Type II ( + ) as the stage diagram has positive incline. A Type III microemulsion stage exists as a distinguishable and bicontinuous 3rd stage with extra oil and H<sub>2</sub>O stages. Type III is a transitional stage between Type I and Type II. The passage of stage

behaviour from Type I to Type III to Type II depends on surfactant type,  
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electrolyte, temperature, oil belongingss etc. The surfactant construction could be characterized with hydrophilic-lipophilic balance ( HLB ) , and the oil belongingss could be characterized by tantamount methane series C figure ( EACN ) , which could assist to categorise the wetting agents and select the right wetting agents for mark reservoirs and petroleum oils.

The most common stage behavior passage from Type I- & gt ; Type III- & gt ; Type II is accomplished by altering electrolytes.

### **Micro-emulsion and Interfacial Tension**

Microemulsion can be characterized in several ways: the sum of water/oil solubilized in microemulsion, the clip for microemulsion to blend, or microemulsion viscousness. Healy and Reed ( 1976 ) define water/oil solubilization ratio by splitting the sum of water/oil solubilized in microemulsion by entire surfactant volume (  $V_w/V_s$ ,  $V_o/V_s$  ) . Water solubilization ratio decreases as salt additions while oil solubilization ratio additions as salt additions. The intersection where the water/oil solubilization ratio curves meet corresponds to optimum salt and optimum solubilization ratio, where water/oil is solubilized the same sum and to the greatest grade for both the H<sub>2</sub>O and oil in the microemulsion stage, i. e.

lowest interfacial tenseness between oil/water and microemulsion. Healy and Reed besides suggest a correlativity between water/oil solubilization ratio and interfacial tenseness ( IFT ) , which was theoretically derived by Chun Huh ( 1979 ) . Chen Huh ' s equation shows that IFT is reciprocally relative to the square of the water/oil solubilization ratio: where C is about 0. 3

dynes/cm for most petroleum oils. Because it is hard and clip devouring to

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mensurate the IFT between water/oil and microemulsion, by utilizing this equation one could rapidly test out the wetting agents giving low solubilization ratios.

Wetting agents organizing complex stages, such as a liquid crystal stage and a gel stage, normally have drawn-out equilibration clip. It takes a really long clip to obtain stabilised solubilization ratio for these wetting agents and they normally have jobs in propagating in the nucleus or reservoir, and therefore they are besides screened out.

## **Chemical Flood Oil Mobilization Mechanism**

Residual oil in the reservoir is trapped by capillary forces and could be mobilized by increasing syrupey forces and/or gravitative forces over capillary forces. The dimensionless footings referred to as capillary figure  $N_c$  and Bond figure  $N_B$  are the ratios of syrupey forces to capillary forces and gravitative forces to capillary forces:

;

Pope et Al. ( 2000 ) defines pin downing figure which is the combination of both capillary figure and Bond figure to qualify the mechanism to retrieve residuary oil.

Because we can make little to increase stone permeableness (  $K$  ), cut downing interfacial tenseness is an effectual manner to increase capillary figure under a normal force per unit area gradient (  $sl_i$  ) . Chemical deluging with wetting agents could cut down interfacial tenseness to every bit low as  $10^{-4}$  dyne/cm, which normally could increase capillary figure low plenty to

mobilise residuary oil the wetting agent contacts. In order to mobilise the residuary oil, capillary figure normally needs to be increased by a factor of 100-1000 times above typical H<sub>2</sub>O inundation ( Abrams, 1975 ) . Delshad et Al. ( 1986 ) show capillary figure demands to increase to be on the order of 10<sup>-5</sup> before residuary oil impregnation will diminish and to be on the order of 10<sup>-3</sup> to cut down residuary oil impregnation to approach nothing for sandstone. Kamath ( 2001 ) shows that due to different pore constructions and wettability, a lower capillary figure, on the order of 10<sup>-7</sup> is required to get down mobilising residuary oil, but requires a higher capillary figure to cut down residuary oil to approach nothing in carbonate than sandstone. Therefore, in a research lab nucleus inundation graduated table, residuary oil after H<sub>2</sub>O inundation in carbonate is normally lower and tends to be more hard to retrieve all residuary oil than in sandstone.

## **EOR Chemicals**

A typical surfactant preparation as an aqueous stage to organize a microemulsion stage with an oil stage normally contains primary wetting agent, co-surfactant, co-solvent, alkali, polymers and electrolytes. The primary wetting agent is the chemical chiefly responsible for solubilizing oil in the microemulsion stage. The co-surfactant is used to better the public presentation of primary wetting agent ( Nelson et al. 1984 ) . The co-solvent is added to the surfactant preparation to cut down equilibration clip and to forestall forming of the gel or crystal stages Another of import function of co-solvent is to do surfactant preparation compatible with polymers ( Pope et al. 1982 ) and to keep surfactant bullet as a stable one stage at reservoir conditions. Alkali could respond with naphthenic constituents in rough oil and

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bring forth unmoved soap to better the solubilizing of oil in the microemulsion stage. It could besides speed up microemulsion coalescence and cut down surfactant surface assimilation ( Jackson 2006 ) .

Polymer is added to surfactant bullet to increase its viscousness and keep mobility control when displacing oil in reservoir. Electrolytes are adjusted to accomplish optimum Type III stage to maximally cut down interfacial tenseness ( increase capillary figure ) and hence achieve high oil recovery.

## **Wetting agents**

Wetting agents are the cardinal constituents in surfactant preparation used to solubilize oil and H<sub>2</sub>O in the microemulsion stage and hence cut down interfacial tenseness between the microemulsion and the oil/water stage.

Wetting agents by and large contain a hydrophilic caput, a hydrophobic tail and possible intermediate impersonal groups.

The constructions of surfactant caput and tail could be tailored for each specific petroleum oil for the highest oil recovery efficiency and are discussed in the undermentioned paragraphs. Wetting agents can be classified into anionic wetting agents, cationic wetting agents, nonionized wetting agents and amphiprotic wetting agents harmonizing to charge of their hydrophilic caput groups. A Anionic and nonionized wetting agents are more normally used EOR wetting agents than others, therefore they are described in following paragraphs.

## **Anionic wetting agents**

Anionic surfactants give rise to a negatively charged surfactant ion ( therefore non-ionic detergent ) and a positively charged counterion upon disintegration in H<sub>2</sub>O. They are the most normally used and most promising wetting agents in chemical EOR because of their first-class public presentation and low surface assimilation in stones. Sandstone atoms normally carry a net negative charge at reservoir conditions, which could forestall pulling anionic wetting agents ( Zhang and Hirasaki, 2004 ) .

The surface charges on carbonate stone atoms are dependent on brine composing and pH ( Churcher et al. 1991 ) . Nevertheless, anionic wetting agent surface assimilation could be reduced by increasing pH to above 8. 5 to alter the surface charge to negative.

Examples of common anionic wetting agents in recent progresss of chemical EOR are alkylbenzene sulfonates ( ABS ) , alcohol ethoxy sulphates ( AES ) , alcohol propoxy sulphates ( APS ) , internal alkene sulfonates ( IOS ) and Guerbet alkoxy sulphates ( GAS ) . ABS wetting agents are conventional wetting agents that were extensively used in the yesteryear. Their advantages are a high solubilization ratio of rough oil and low optimum salt due to strong hydrophobicity from the benzene aromatic ring and alkyl concatenation. Their aqueous solubility, nevertheless, is low and they tolerate merely low hardness ( Jackson, 2006 ) . Therefore, they can merely be injected into the formation with fresh H<sub>2</sub>O or low salt seawater, or used as a co-surfactant to increase the hydrophobicity with a co-solvent to better its solubility. IOS wetting agents have proved to be first-class EOR wetting

agents ( Levitt, 2006 ; Jackson, 2008 ; Flatten, 2008 ) , peculiarly as co-surfactants that improve the compatibility between the primary wetting agent and the aqueous stage through its structural heterogeneousness of bifurcate big C ironss.

AES/APS are sulfates incorporating ethylene oxide ( EO ) or propylene oxide ( PO ) groups. EO and PO groups are intermediate map groups that attach to the C concatenation and have opposite effects. For illustration, increasing EO groups will increase surfactant aqueous solubility, Ca tolerance and optimum salt while increasing PO groups has the contrary consequence. The figure of EO/PO groups determines the hydrophilicity and hydrophobicity of wetting agents and they can be tailored specifically for different petroleum oils.

This flexibleness of wetting agents widens the scope of their application in chemical EOR. GAS wetting agents are anionic wetting agents, which can be manufactured in a comparatively cheap manner that are produced by add-on of ethylene oxide and/or propene oxide to the blend of Guerbet intoxicant and monomer intoxicant instead than pure Guerbet intoxicant. With really big hydrophobes and branched constructions to obtain ultra-low interfacial tensenesss and low micro-emulsion viscousnesss ( Liu et al.

2007 ) , GAS can be used for petroleum oils with tantamount methane series C figure higher than 12. The hydrolysis of GAS wetting agents can be mostly reduced at certain alkalinity scope at high temperatures, which could heighten surfactant stableness, and hence do GAS wetting agents able to be used in high temperature reservoirs ( Adkins, et Al. 2010 ) .

## **Nonionized wetting agents**

Nonionized wetting agents do not ionise in aqueous solution because their hydrophilic group is of a non-dissociable type, such as intoxicant, phenol, ether, ester or amide. The advantages of nonionized surfactants are that they are normally easy blended with other types of wetting agents and are comparatively insensitive to the salt of the solution. A big proportion of these nonionized wetting agents are alcohol ethoxylates, which are made by the polycondensation of ethylene oxide. Alcohol ethoxylates could be used as co-solvents that could replace conventional solvents in greatly lessened sums ( Sahni et al.

, 2010 ) . Nonionized wetting agents, such as intoxicant ethoxylates, nevertheless, normally have high optimum salt and their use is limited due to comparatively low cloud point, i. e. , aqueous solubility ( Milton, 2004 ) .

## **Co-solvents**

Co-solvents are by and large used in surfactant preparation to increase the compatibility between wetting agents and the aqueous stage, and hence increase its thermic stableness.

Achieving a clear and stable surfactant bullet is of import to guarantee the injected solution will transport in the reservoir over long distances with low keeping ( Sahni et al. , 2010 ) . Co-solvent besides helps to cut down or extinguish the syrupy stage and accelerate microemulsion equilibration ( Sanz and Pope, 1995 ) . Co-solvents are normally amphiles and have the ability to divider into aqueous stages, and oleic and microemulsion stages, which allows co-solvents to alter stage behaviour ( Dwarakanath et al.

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, 2008 ) . For illustration, hydrophilic co-solvent additions optimum salt and lipotropic co-solvent reduces optimum salt while both addition aqueous stableness. Alcohols are one of the widely used conventional dissolvers. Branched construction alcohols incline to supply better hydrophilicity than additive construction intoxicants for the same molecular weight ( Hsieh and Shah, 1977 ) .

Common intoxicants used in EOR include iso-propanol ( IPA ) , iso-butanol ( IBA ) , sec-butonal ( SBA ) and so on. Glycol quintessence intoxicants are assuring co-solvents because of their first-class ability to do wetting agents compatible with the aqueous stage at high salt ( Sahni et al. 2010 ) and their higher flash point. The disadvantage of utilizing co-solvents is that it reduces the solubilization ratio of water/oil and accordingly increases interfacial tenseness ( Salter, 1977 ) , and it besides surely increases chemical cost. It is possible to accomplish high oil recovery with intoxicant free wetting agent preparation ( Sanz and Pope, 1995 ) . Alcohol can besides be replaced by other chemicals, for illustration intoxicant ethoxylates, which can give better aqueous stableness and higher optimal salt at low concentrations.

For active oil, which contains sufficient naphthenic acid to bring forth soap with base, a hydrophilic wetting agent is sufficiently soluble in seawater at optimum salt without the demand for any co-solvent or merely a little sum of co-solvent. For inactive oil, wetting agents with big hydrophobes are frequently needed to accomplish a high oil solubilization ratio and low IFT. These wetting agents are less soluble in seawater, and therefore they need a comparatively big sum of co-solvents to obtain aqueously stable surfactant

bullet. In amount, intoxicant concentration needs to be determined in such a manner to equilibrate the microemulsion viscousness, equilibration clip and the solubilization ratio for maximal preparation public presentation and highest oil recovery.

## **Base**

Alkali has been observed to better surfactant stage behaviour and oil recovery in nucleus inundation experiments ( Nelson et al. , 1984 ; Wellington and Richardson, 1997 ) .

The mechanisms behind this are:( 1 ) Alkali reacts with naphthenic acids in rough oil in-situ and produces natural wetting agent. Natural surfactant normally is non plenty to cut down interfacial tenseness and demands to work together with man-made wetting agent in chemical inundation.

Besides, natural wetting agent has comparatively low optimum salt ( alkali concentration ) and man-made wetting agent could be added to raise optimum salt to set surfactant preparation to the appropriate base concentration needed to propagate in the reservoir ( Nelson et al.

, 1984 ) . In phase behaviour experiments, the natural wetting agent from saponification naphthenic acid additions optimum solubilization ratio with even mildly or decrepit reactive petroleum oils. Conventionally the entire acerb figure, which is the sum of K hydrated oxide in mgs that is needed to neutralize the acids in one gm of oil, is a good index of naphthenic acids that can be saponified. Saponification figure, nevertheless, should be measured to find the entire sum of soap that could be generated by an alkali reaction ( Yang et al.

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, 2010 ) . Heavy oil tends to hold higher entire acid figure than light oil and can profit more from base.( 2 ) Promoting pH by adding base could cut down surfactant surface assimilation by increasing negative charges on sandstone stone ( Nelson et al. , 1984 ; Wessen and Harwell 2000 ; Zhang and Somasundaran, 2006 ) . Low surfactant surface assimilation promotes surfactant slug extension ( Nelson and Pope, 1977 ) and enables low surfactant concentration chemical implosion therapy. Alkali in surfactant preparation besides improves the coalescency clip of microemulsion in stage behaviour experiments ( Castor, 1981 ) , which indicates low viscousness of the microemulsion stage ( Nelson et al.

, 1984 ) and facilitates quickly mobilizing oil and development of the oil bank in-situ. The decrease of microemulsion stage viscousness and attendant betterment of fluidness can cut down the sum of intoxicant needed. Sodium carbonate is a conventional base in chemical inundation. In the presence of gypsum or anhydrite, which is frequently the instance with dolomite stones, nevertheless, carbonate ions and Ca ions precipitate as Ca carbonate ( Labrid, 1991 ) . Sodium metaborate is an alternate base that prevents precipitation of Ca carbonate by organizing soluble composites with dissolved Ca ions and borate ions ( Flaaten et al. , 2006 ) . Tetrasodium ethylenrdiamine tetraacetate ( EDTA-4Na<sup>+</sup> ) is another promising base which acts as a chelating agent to sequester metal ions such as Ca and Mg ions with its two aminoalkanes and four carboxylates ( Yang et al. , 2010 ) .

## Polymer

Polymer is chiefly used to increase the viscousness of surfactant bullet and to therefore provide adequate mobility for stable supplanting of the oil bank by surfactant bullet in chemical implosion therapy ( Sorbie, 1991 ; Willhite and Green, 1998 ) . Increasing the viscousness of the surfactant bullet additions sweep efficiency by cut downing or extinguishing fingering, peculiarly in heterogenous reservoirs. Polymer is frequently needed in both surfactant bullet and polymer thrust, which protects the unity of surfactant bullet. The viscousness of slug/drive ( depends on amount/molecular weight of polymer ) of stable supplanting is determined in such a manner that mobility ratio is maintained to be less than one ( Gogarty et al. , 1968 ) . Partially hydrolyzed polyacrylamides ( HPAMs ) are conventional polymers which are susceptible to debasement by shearing every bit good as thermic debasement. The effects on stableness of HPAM by assorted factors such as temperature, initial grade of hydrolysis, sum of divalent cations, pH, and dissolved O are examined by Shupe ( 1981 ) and Moradi-Araghi ( 1987 ) . Xanthan gum, a bacterial polyose, has a stiff construction, which yields important opposition to shear debasement compared to HPAMs.

It has the advantage of being insensitive to salt and bivalent cations due to its stiff construction and deficiency of an anionic group. It, nevertheless, is susceptible to bacterial debasement. Although xanthan gum was loosely used in early chemical inundations, HPAMs are more normally used in recent chemical inundations.



## Core Flood Design

Lab nucleus inundations are efficient ways to formalize the public presentation of surfactant preparation that shows good stage behaviour consequences before field application. Residual oil trapped in the nucleus after H<sub>2</sub>O implosion therapy is the mark of chemical implosion therapy. The highest capillary figure corresponds to the lowest IFT for both oil-microemulsion and water-emulsion stages, which is achieved at the optimum salt of surfactant preparation. Therefore, surfactant bullet with optimum salt is normally injected into the nucleus. Surfactant bullet with over optimum salt thrusts surfactant into the oil stage doing surfactant loss and leaves oil trapped once more even though the oil is mobilized by microemulsion due to low oil-microemulsion IFT.

Surfactant bullet with under optimum salt still has comparatively high oil-microemulsion IFT and hence can non mobilise oil. For coreflooding, the seawater salt in the nucleus could be good controlled to accomplish optimum salt in order to broaden the surfactant Type III part with low IFT. In the field, nevertheless, reservoir salt normally is non optimum salt, and it is hard to accomplish optimum salt everyplace because of ( 1 ) wetting agent slug scattering with reservoir seawater ; and ( 2 ) optimum salt is a map of altering surfactant concentration.

Pre-flush of optimum salt seawater is often un-necessary, and even damaging to oil recovery ( Pope et al. , 1979 ) . A robust chemical inundation design which uses a salt gradient is proposed by Pope et Al. ( 1979 ) , where the salt downstream of the bullet is higher than optimum salt, at the bullet is

equal to optimum salt and upstream of the bullet is lower than optimum salt. This salt gradient design greatly increases the opportunities of surfactant bullet passing by optimum salt and advancing low IFT at least someplace in the commixture zone. Over optimum salt downstream besides helps mobilise oil and under-optimal salt upstream helps forestall surfactant or mobilized-oil from being trapped.

## **Crude Oil Evaluated**

The petroleum oil used in this survey is Wahrman rough oil, from a limestone reservoir located in the northwest portion of Kansas. Reservoir temperature is about 43.3 A°C ( 110 A°F ) . It has low viscousness, 7.5 cP ( filtered ) at reservoir temperature and is light ( API gravitation: 37.

9 at reservoir temperature ) . It has low acid figure, approximately 0.014 g KOH/g ; hence there is small naphthenic acid in Wahrman petroleum oil to bring forth natural wetting agents with reaction of Na carbonate.

The formation seawater contains 12 wt % TDS including 2500ppm bivalent ions.