Surfactants and other factors input for the control of the reservoir interfacial tension (IFT).

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Outlines

- Introduction.
- Objectives
- Surfactants Screening-Solutions Preparation
- Experimental work on application of selected surfactant in the recovery mechanism (EOR)
- Results and discussion
- Conclusions and Recommendations

Target

The Investigation is aimed to assess:

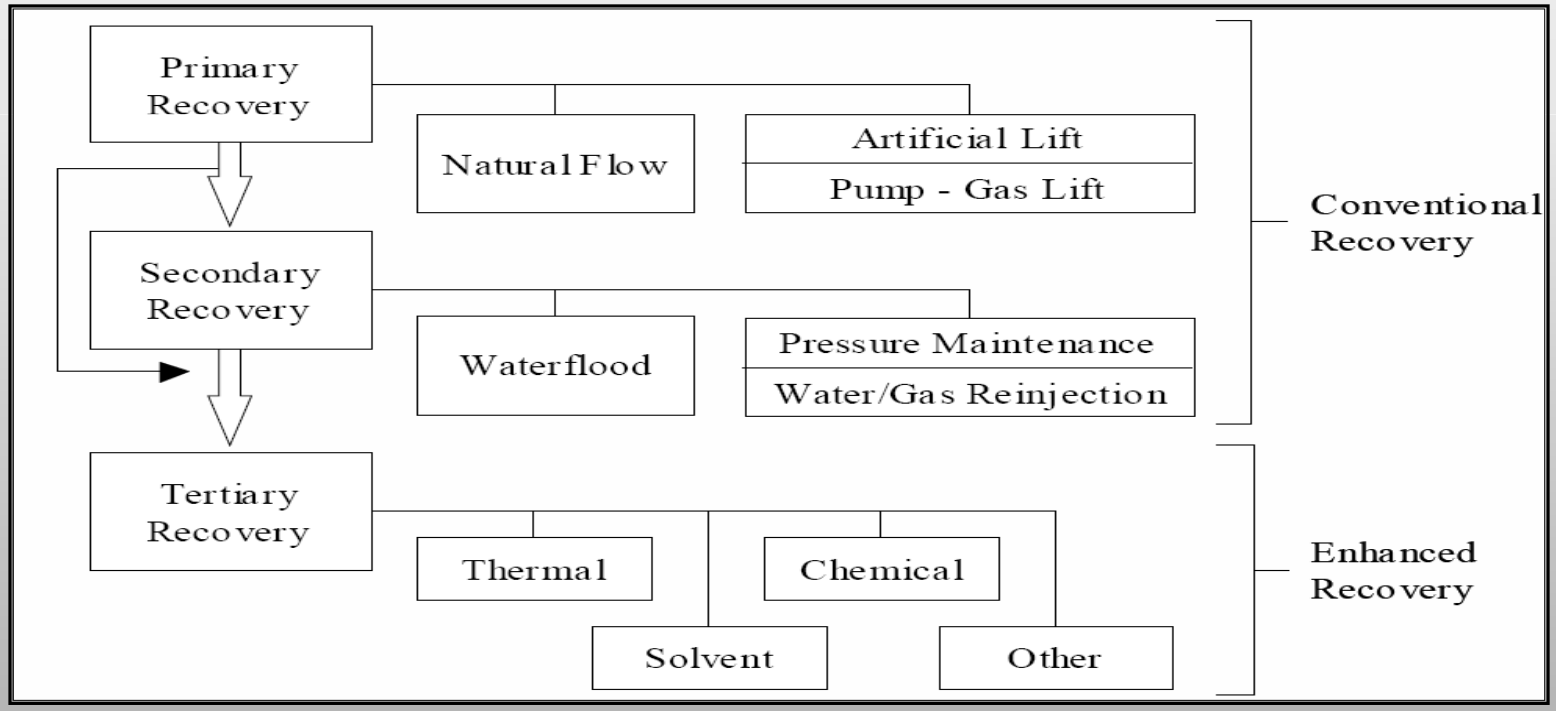
- Investigation on The Interfacial Tension under the following conditions:
- Pressure, temperature and salinity in the change of the IFT (Interfacial Tension)
- CMC (Critical Micelles Concentration).
- Surfactant Flooding based on the screened ones will be the achievement.
- The case of Saudi crude oil was approached in that regard up to the reservoir conditions

Introduction

- Oil and service companies have invested a lot in increasing recovery and productivity
- The amount of unrecoverable oil is limited by existing recovery mechanisms, efficiency economic condition and technology applications.
- Enhanced Oil Recovery (EOR) processes remains a vital issue .
- The Use of Surface Active Agents (chemical surfactants) prior to any other steps can be set as essential in the recovery improvement issue.

EOR Target (General Flow Chart)

EOR is targeting an increase of the reserves by retrieving the remaining 50-70% left by primary and secondary recovery methods as indicated in the following scheme.



Why the Use of Surfactants ?

Among Surfactants selected properties:

- Friendly to the environment,
- Low cost and commercially available,
- Noncorrosive,
- Recyclable,
- Thermally stable,
- Nonflammable,
- Nonvolatile,

Applications of Surfactants in Petroleum Industry

- Upgrading heavy crude oil.
- Extracting crude oil e.g. from tar sands .
- Cleaning costal areas from spilled crude.
- Extraction of contaminants such as Sulfur and Nitrogen from crude oil.
- Prevention of asphaltene precipitation in Transportation and at last,
- Enhanced Oil Recovery (EOR).

Methods

- Surfactants screening based on solubility, stability and ability to reduce IFT.
- IFT measurement using pendent drop method.
- CMC Determination (Critical Micelle Concentration)

Equipments

- Pendent drop tensiometer (Automatic and manual)
- Drop shape analysis tensiometer for IFT measurements (DSA 100)
- DMA4500 Anton Paar density meter and Cambridge viscometer (crude oil density and viscosity measurement respectively).
- CFS-830 Fully automated flooding unit.

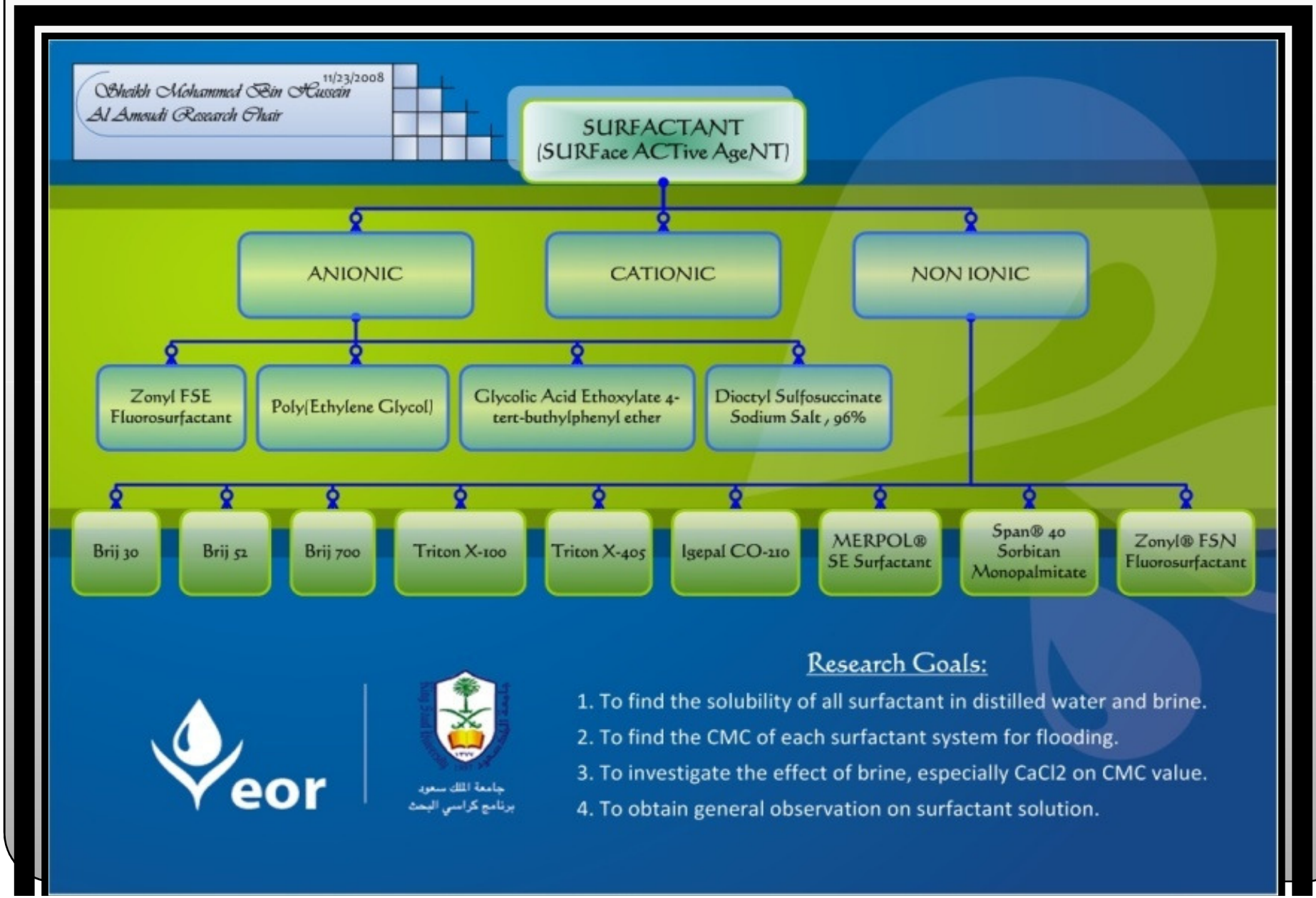
Material and Procedure

- Saudi medium crude oil (API = 28.37).
- Brine composed of NaCl & CaCl2 salts dissolved in distilled water at different concentration).
- Several screened Surfactants
- Berea sandstone core samples.

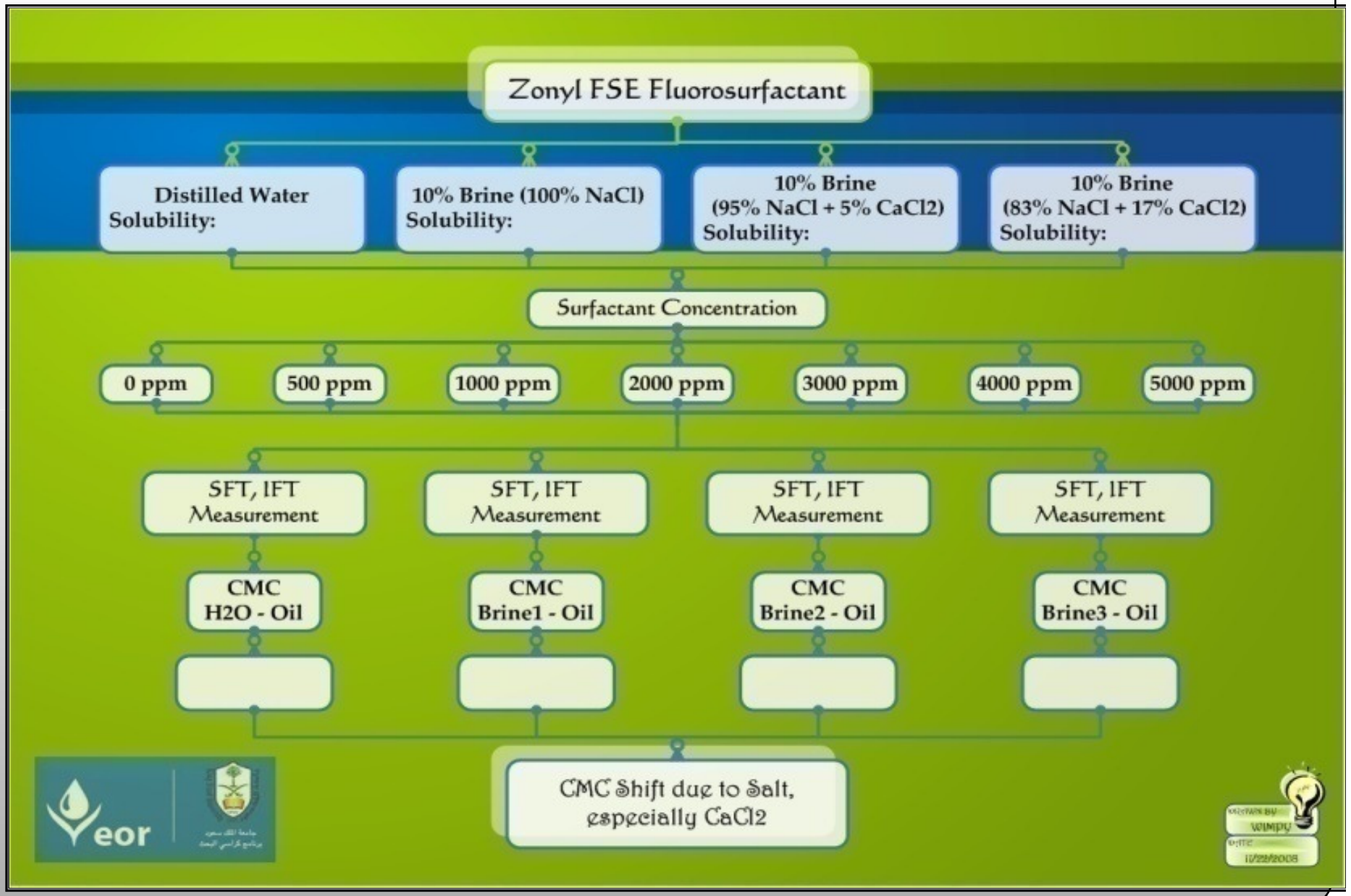
Surfactant utilized in this investigation and their Properties

Surfactant	Zonyl FSE Fluorosurfactant	Triton X-100	Triton X-405
Type	Anionic	Nonionic	Nonionic
Synonym/Molecular Formula	Ammonium bis [2-(perfluoroalkyl) ethyl] phosphate	4-$(C_8H_{17})C_6H_4(OCH_2CH_2)_nOH$, n~10	Polyethylene glycol *tert*-octylphenyl ether
Density	1.1 gm/mL at 25 °C(lit.)	1.07 gm/mL at 25 °C(lit.)	1.05 gm/mL at 25 °C(lit.)
HLB	-	13	17.9
Working Temperature (°C)	Tested stable until 90 in purified water and brine	<60 in purified water; <40 in brine solution	tested stable until 90 in purified water; <60 in brine solution

Surfactants utilized during the Investigation and their Properties



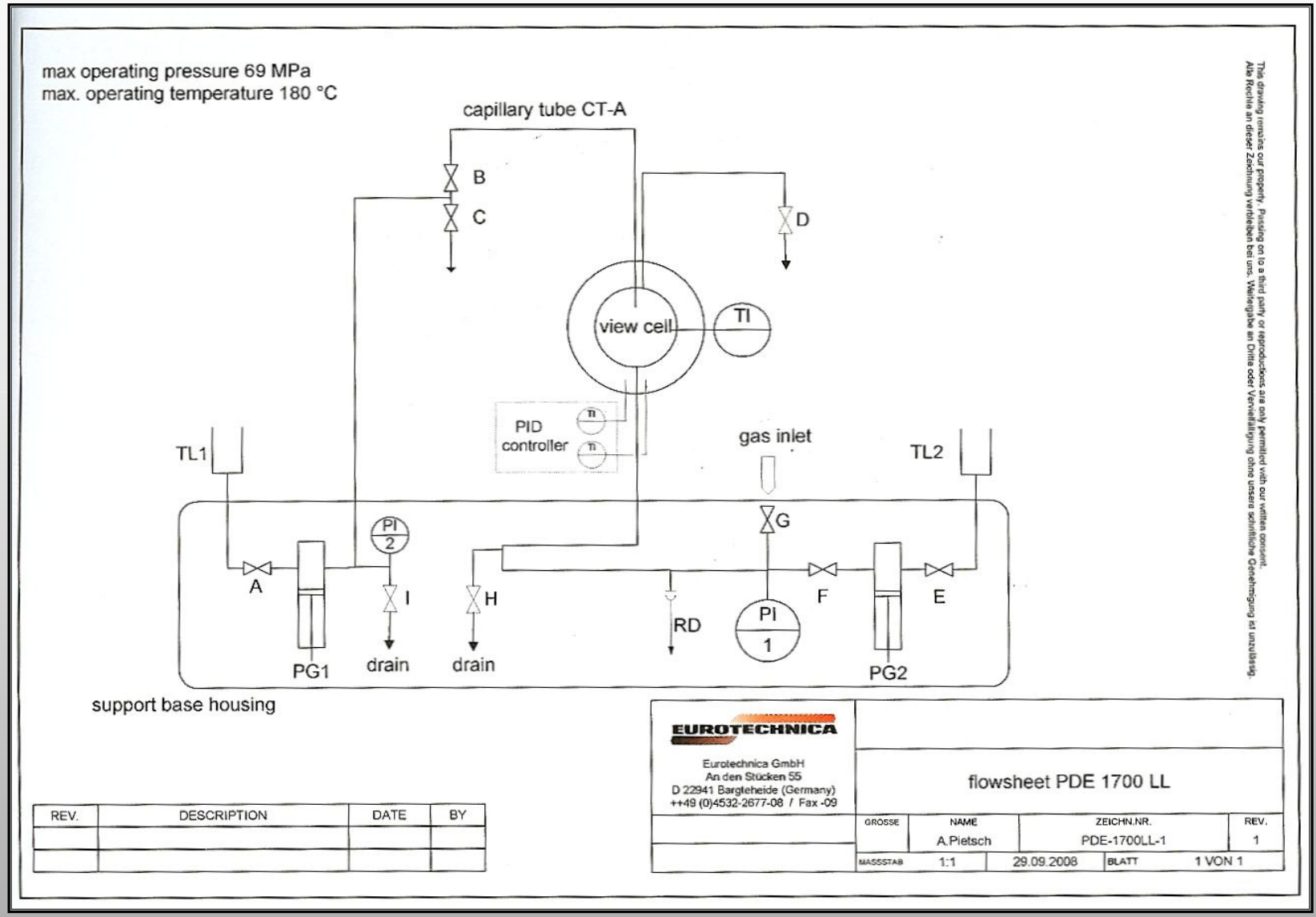
Experimental Procedure (Flow Chart e.g. Zony FSE and Brine Type)



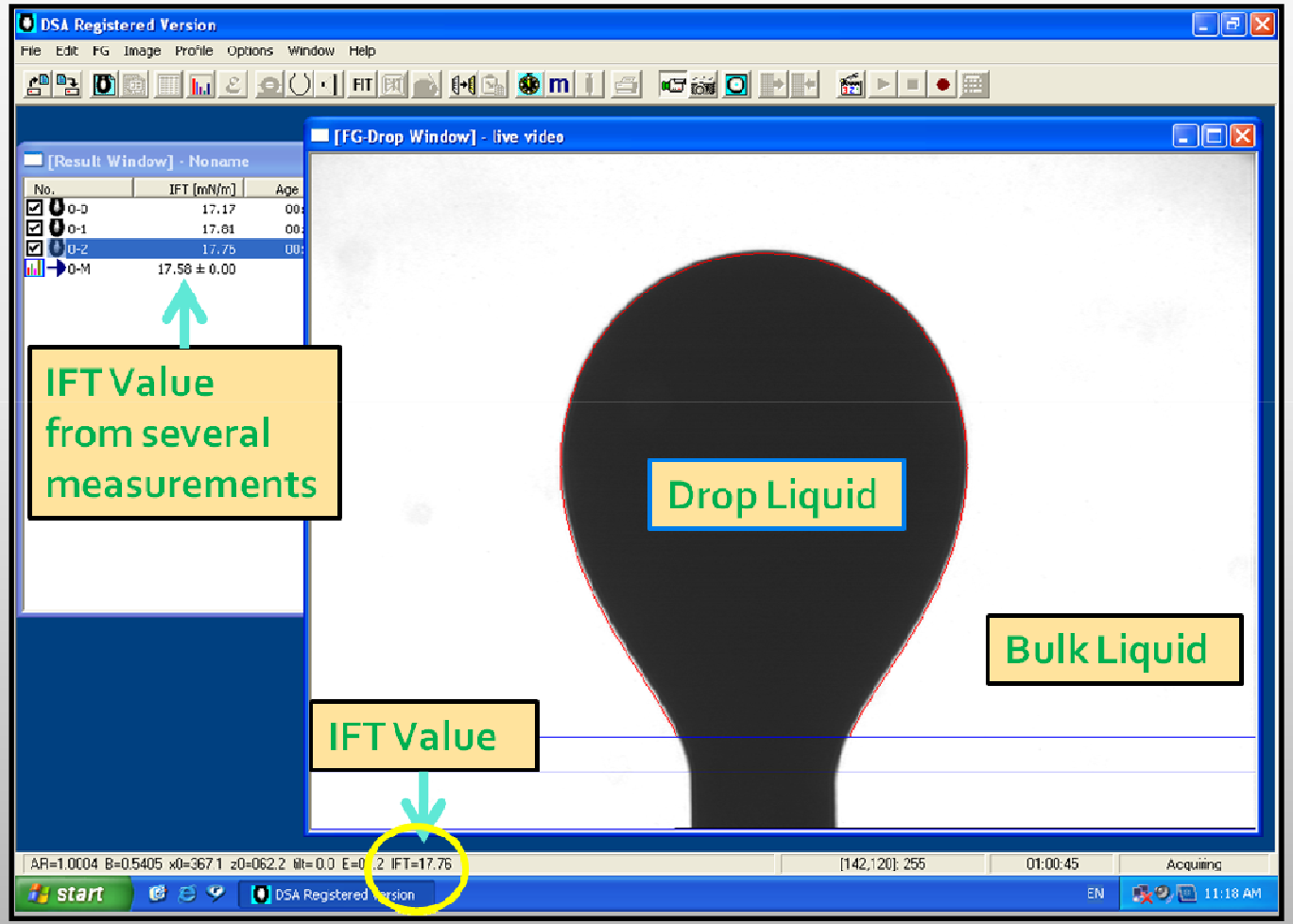
Experimental Work (Exhaustive Flow Chart)

- The same experimental sequence was conducted for the two other selected surfactants studied (Triton 405 and Triton X 100)
- Flow chart consists on steps of prepared solutions leading to IFT measurements (e.g. Zonyl FSE.
- Selected surfactants is based on screening.
- The same sequence was conducted for the two other screened surfactants (Triton X 100 and Triton X 405).

Flowsheet for *Measuring IFT Using DSA100*



IFT Measurement (Drop Liquid/Bulk Liquid)



IFT Measurement Procedure

All samples were measured as:

- five IFT measurements of different oil droplets were recorded

Measurements were made at different:

- pressures,
- temperatures
- Salinity
- bulk phase solution type and concentrations

Flooding Experiment Procedure

- Saturated sample placed in the core holder
- confining pressure of 4000 psi and pore pressure of 2000 psi were applied providing an effective pressure of 200 psi.
- Brine solution, surfactant solution and crude oil were poured inside the accumulators and the system temperature was raised up to 60 °C.

Results and Discussion

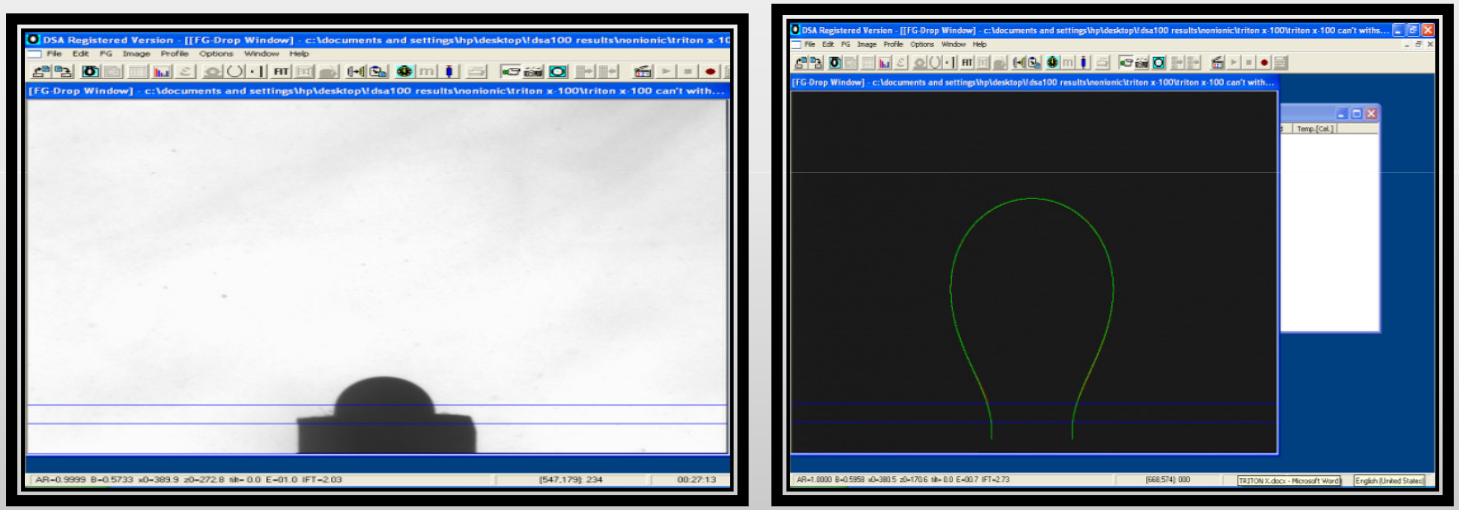
In this investigation,

- Pure water and 10% by weight brine solutions of different NaCl and $CaCl_2$ salt concentrations were used
- Preparation of surfactant solution at different concentrations were made
- Solutions are ranging from from 500 to 4000 ppm by weight.
- Only surfactants with good solubility in both water and brine have been screened and
- Zonyl FSE, Triton X-100 and Triton X-405 were selected .

Drop/ Bubble conditions for IFT measurement (Pendant drop/ DSA)

- Rising bubble
- The bulk phase must be clear and transparent to:
- Enabling the camera to capture the drop image.
- The drop/bubble must have sufficient contrast with the bulk phase to allow the image processing software differentiate them by creating boundary line and hence calculate the IFT value based on the drop/bubble size.
- Uniform solution without solid precipitation is important prior to preventing any throat plugging in core flooding process.
- Thus, accurate results can be achieved.

Illustration for IFT Measurement Restrictions

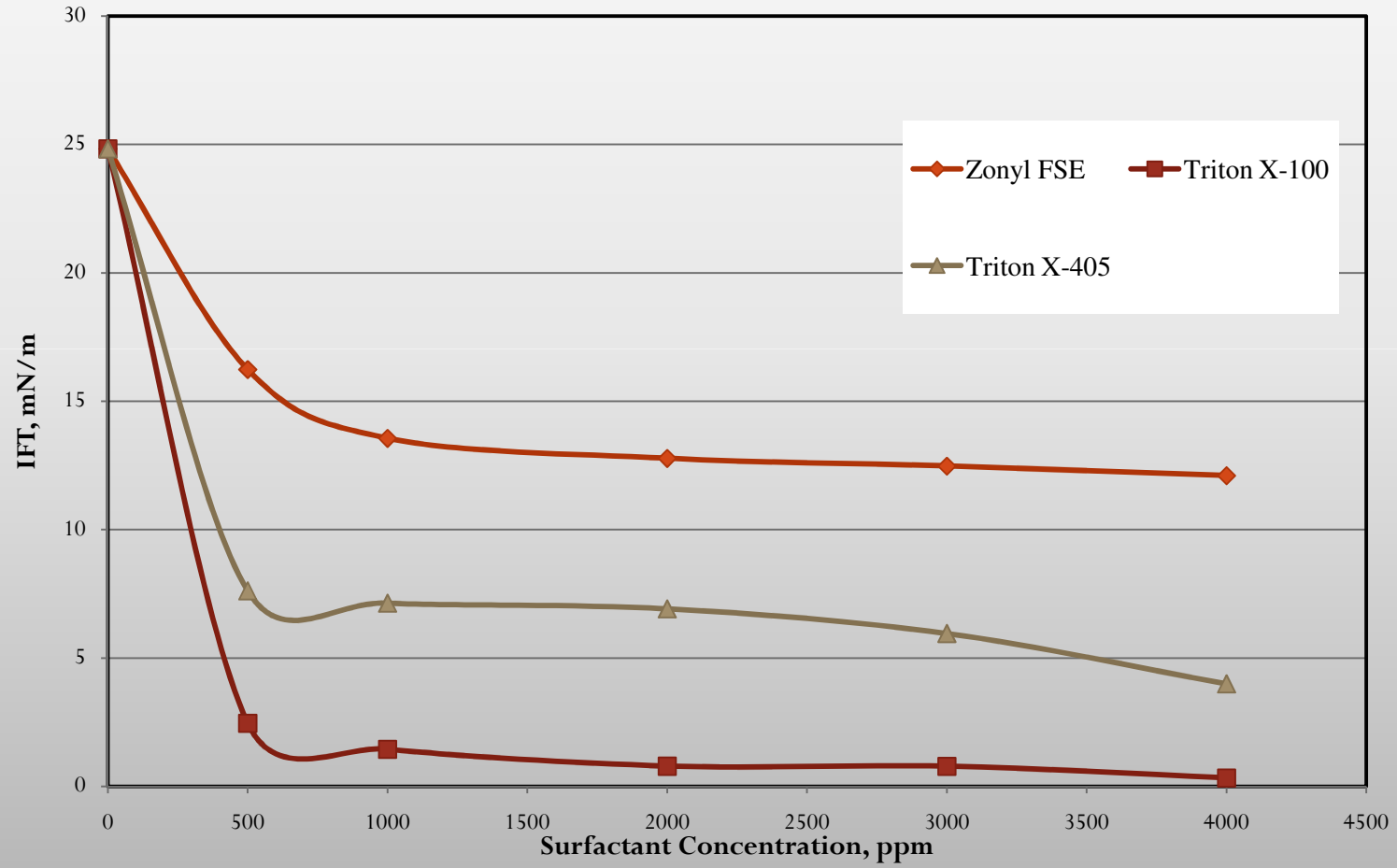


Transparent Measurable Solution (Left) and Dark Cloud Solution causing the measurements impossible (Right)

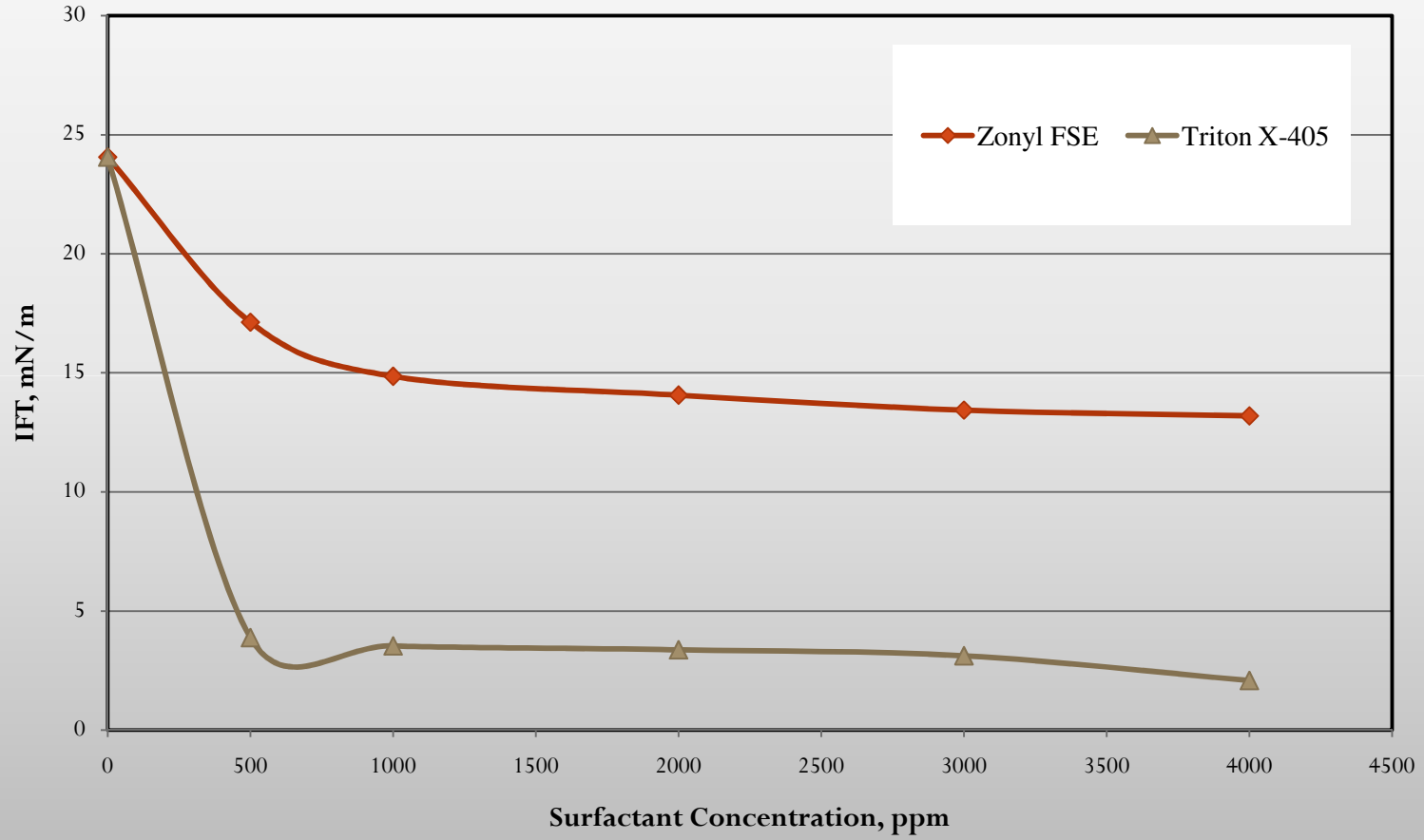
Effect of Surfactant Type and Concentration on IFT

- The effect of surfactant on IFT values with crude oil were measured.
- concentration on IFT for the three surfactants diluted in 83% NaCl and 17% $CaCl_2$
- At 2000 psi pressure and extreme temperatures of 23 and 60 ºC decline infection with the increase of surfactant concentration.
- At certain stage, the drop becomes very slight: the inflection point is referred to as critical micelle concentration (CMC)
- The CMC is known to be the economical concentration for surfactant flooding.

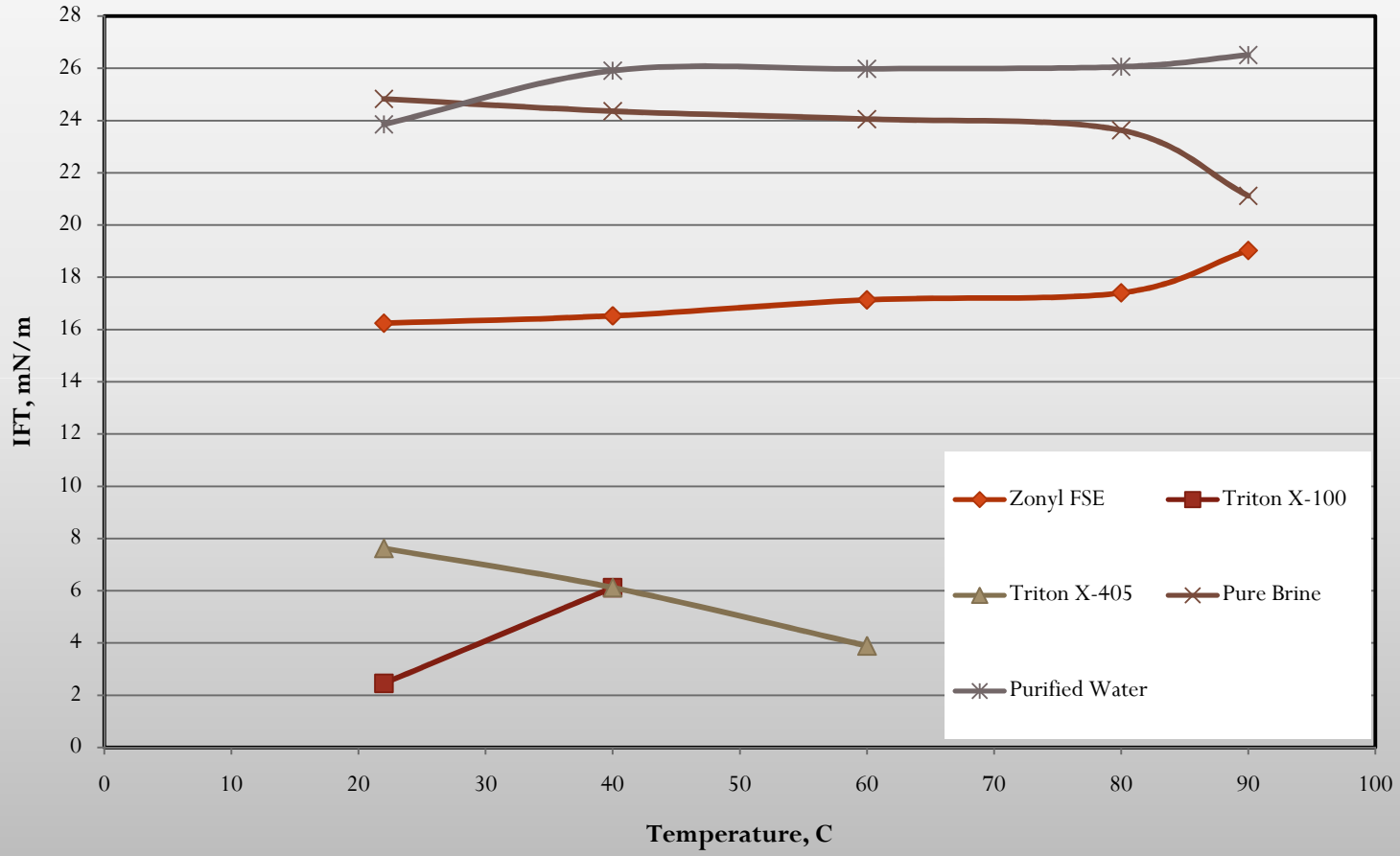
Surfactant Types and Concentration V.S. IFT (reaching the C.M.C Concentration)



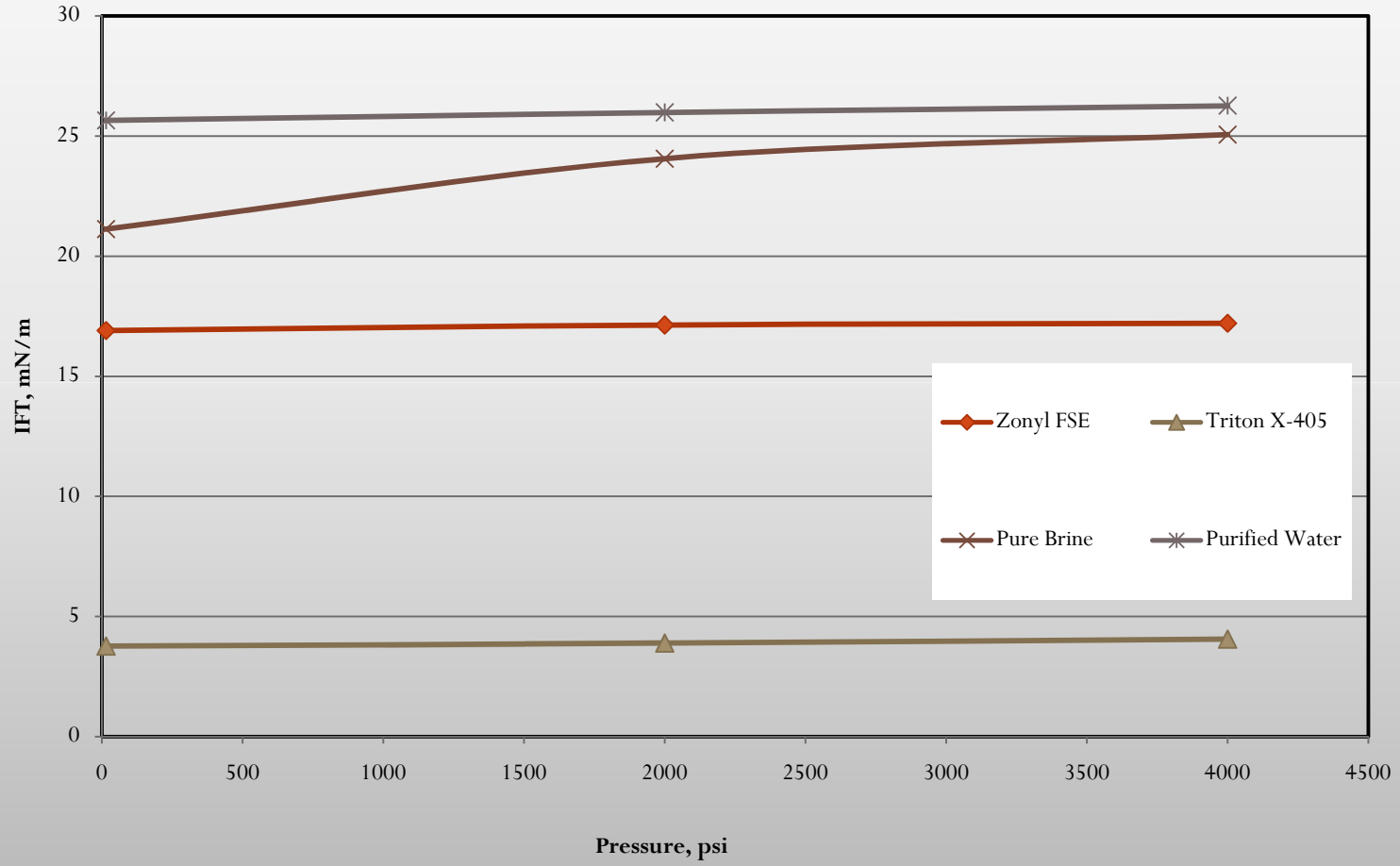
Effect of Surfactant Concentration on IFT for Different Surfactants at 60° C



Effect of Temperature on IFT for Crude Oil-Different 500 ppm Surfactant Solutions at 2000 psi



Effect of Pressure on IFT

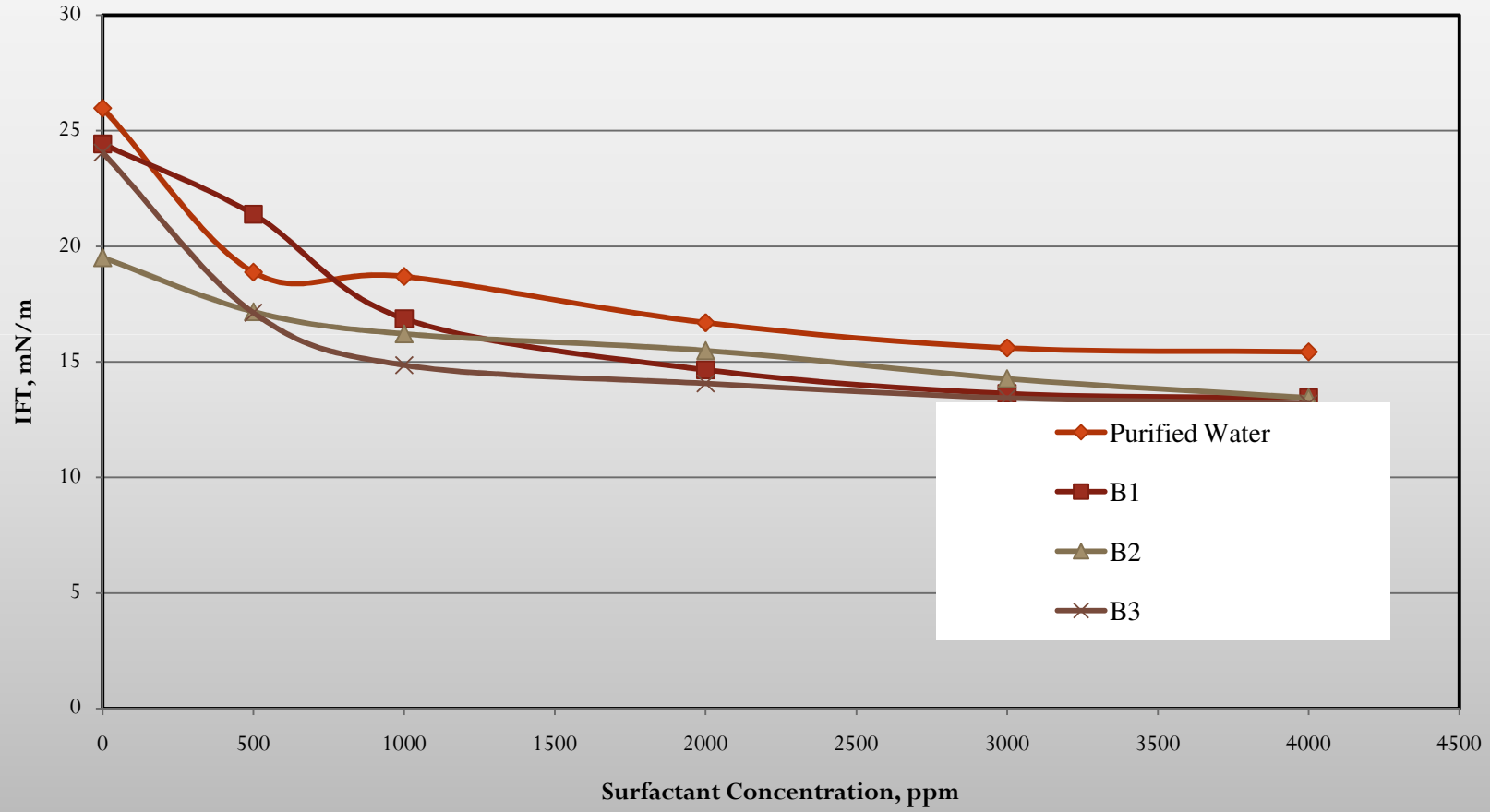


Effect of Salinity and Brine Composition on IFT

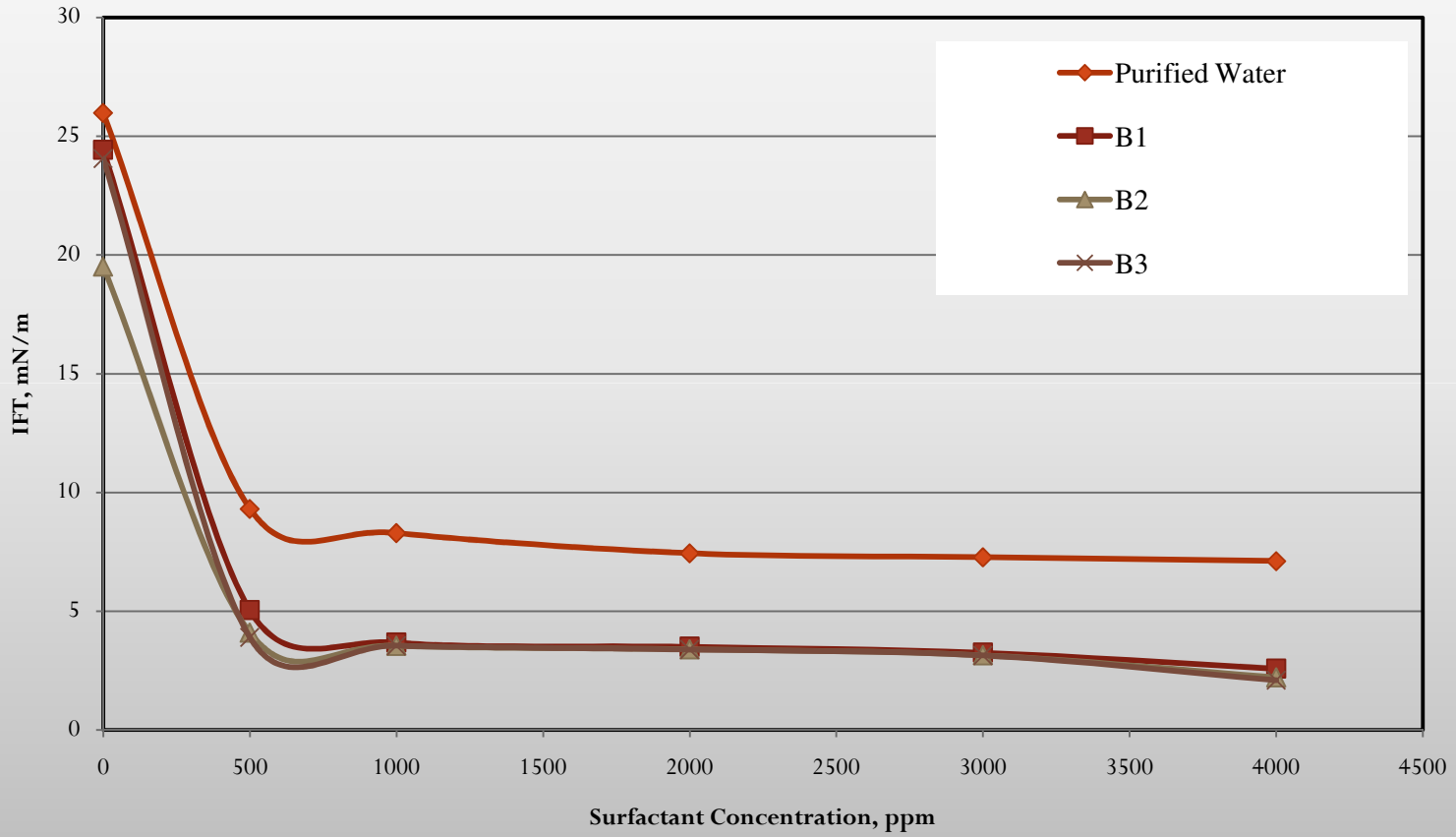
Investigating on the effect of surfactants concentrations on IFT measurements in presence of different brine compositions,

- IFT values measured for Zonyl FSE and Triton X-405
- Solutions were taken at different concentrations at reservoir conditions of 2000 psi and 60 °C.
- Triton X-100 was immeasurable at that temperature of 60°

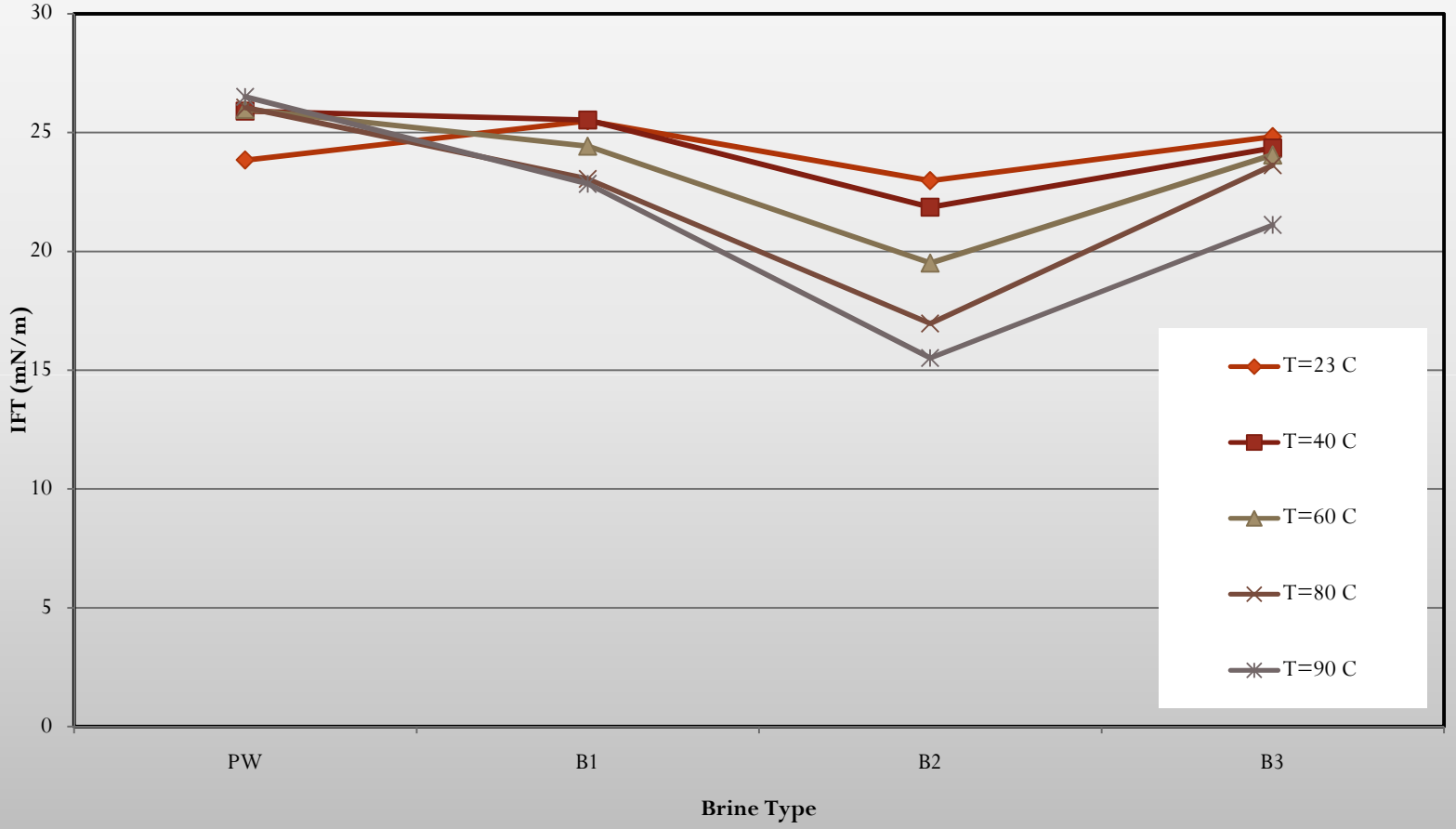
Effect of Surfactant Concentration on IFT for Crude Oil-Zonyl FSE Diluted in Different Brines at 2000 psi and 60 °C



Effect of Surfactant Concentration on IFT for Crude Oil- Triton X-405 Diluted in Different Brines at 2000 psi and 60 °C



Effect of Brine Salinity Composition on IFT at Variable Temperature Conditions



Results -Interpretation

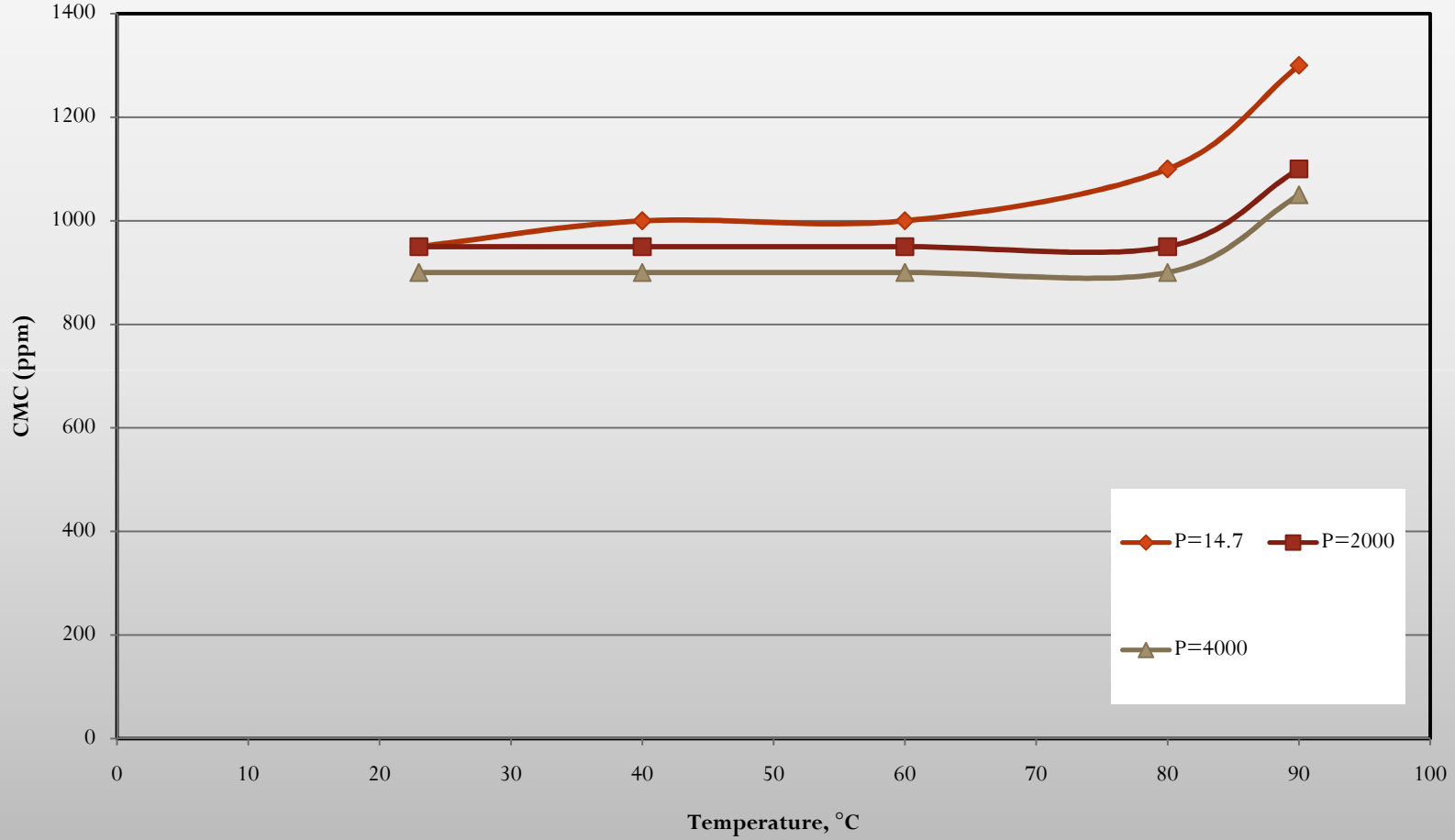
According to the obtained Graphs

- Results indicate exponential IFT decline with the increase of concentrations (500, 1000, 2000, 3000 and 4000 ppm @ 10% brine)
- Relatively more drop on IFT values in presence of salt in solution.
- The drop is more radical for Triton X-405 than that for Zonyl FSE
- Thus, effect can be favorable for surfactant flooding suggesting : Triton X-405 to be more efficient for chemical flooding at reservoir conditions of pressure, temperature and salinity conditions compared to the Zony FSE.

Critical Micelle Concentration (CMC) Results

- CMC values of Zonyl FSE and Triton X-405 surfactant solutions at different temperatures and pressures.
- Results indicate no effect for temperature and pressure for Triton X-405, however,
- CMC of Zonyl FSE solutions decreases with increasing pressure and levels out with increasing temperature
- Exception is at higher temperature above 80 °C where CMC values are enhanced (Zonyl FSE).

Effect of Temperature on CMC of Zonyl FSE at Variable Pressure Condition in 10% Brine (83% NaCl + 17% $CaCl_2$)



CMC (Critical Micelle Concentration) Interpretation

According to the obtained results:

- salt composition effect on CMC values of Zonyl FSE and Triton X-405 at 60 °C and 2000 psi is erratic.
- No effect of salt composition on CMC values for Triton X-405.
- Contrary, significant effect of salt composition on CMC was seen for Zonyl FSE fluorosurfactant.

Flooding Results

- At experiment conditions of pressure, temperature and surfactant concentration (CMC),
- Triton X – 100 IFT with predicted Recovery (due to the dark solution phenomenon faced during the measurement) has IFT around 6 to 7 Mn/m
- Triton X-405 fluid pair has an IFT of 3.54 mN/m
- Triton X-405 surfactant solution was more efficient recovering 52.3 % OOIP compared 44% OOIP for Triton X-100 solution.

Conclusion

- Triton X-100 cannot withstand temperature above 40 °C, Triton X-405 cannot survive above 60 °C, while Zonyl FSE Fluoro surfactant can resist up to 90 °C.
- At reservoir temperature, (considered at 60 °C), Triton X-405 gives the lowest IFT values, even though at room temperature, Triton X-100 gives the lowest IFT values.
- The presence of salt in the solution can decrease slightly the surfactants IFT value.
- The effect of temperature on IFT is relatively greater compared to the effect of pressure at the same solution and experiment conditions.
- The effects of temperature on IFT are variable which depend on the surfactant.
- Temperature effect on IFT, in brine solution is lower compared to in purified water.
- The effects of pressure on IFT are variable which depend on the surfactant. .

Conclusion

- For Zonyl FSE Fluorosurfactant, as temperature increases the CMC also increases.
- At higher pressure this effect is lower except at temperature above 80 degrees.
- While For Triton X-405, the effect of temperature on CMC is not significant.
- For Zonyl FSE, the CMC decreases as pressure increases.
- The pressure effect is more significant at high temperature.
- While for Triton X-405, the effect of pressure on CMC is not significant

Recommandations

- Laboratory experiments are strongly in need for surfactants properties investigation prior to any application in the flooding process .
- Chemical components or molecules are well appreciated in the regard of their polarity, thus an investigation in that way becomes attractive
- Solution concentration and type, since, the CMC value increases might be due not only to salinity increase but also for the type of it e.g. $CaCl_2$ (divalent ions percentage increases), have to be screened and investigated in the purpose.
- The presence of divalent ions might promote the CMC formation
- Thus, Focus on chemical composition and their valency related to each other request an attractive and better enquiry topics
- In addition The use of any chemicals to enhance the fluid circulation in the reservoir is limited to pore size entry. Thus, size of the chemical particles should be assessed prior to pore size entry

Appreciation

- My Thanks will go to KSU - Petroleum Eng Department -Al Amoudi EOR Chair For the Project Achievement (Riyadh-KSA).

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- My credit will be conducted to the Algerian University of OEB (Larbi Ben M hidi) for allowing me to be among you.

Thank You For
Your Attention