SURFACTANT PROPERTIES EVALUATION FOR CHEMICAL FLOODING

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ABSTRACT

The need of EOR techniques in the late field production period is essential to get the third wind of incremental oil. Chemical injections are proven technologies not only at the laboratory scale but also at the field scale which have been implemented in many parts of the world. Surfactant is an important chemical in this technology, which mostly has been used to reduce the capillary trap of the oil in the reservoirs.

The selection of surfactant type which is suitable for a specific oil field to increase the oil production should fulfill the selection criteria. Laboratory works firstly should be done to evaluate the important properties based on the industrial standard procedures. These laboratory tests include compatibility test, aqueous stability test, phase behavior study, micro-emulsion viscosity, interfacial tension determination, thermal stability test, and filtration test.

Key words : enhanced oil recovery, chemical injection, winsar type III - micro-emulsion

I. INTRODUCTION

After completing a water flood activity, the cumulative oil production of a typical oil field is still very low approximately 30 to 40 percents of the original oil in place only. Therefore, the need of enhancing oil recovery (EOR) techniques is unquestionable. The selection of appropriate EOR methods that will be applied to particular field, as an effort to increase oil recovery, mainly depends on the reservoir characteristics and fluid behavior. Chemical injection such as ASP (alkaline-surfactant-polymer mixture) has been categorized as an effective EOR method in low oil gravity oilfields. Surfactant at low concentration could reduce the interfacial tension (IFT) to oil much lower and capable to overcome the capillary trapped oil. Chemical injection may become the best option in many cases compared to gas injection. Gas injection is normally suitable for deep reservoirs in order to achieve the minimum miscibility pressure without causing fractures formation.

Basically chemical injection includes alkaline, surfactant, polymer injection. They can be arranged to be injected into a reservoir as a series of order injection fluids but also possibly stand alone fluid injection. Nowadays this technology has become simpler by introducing a new injection technique by mixing those chemicals at the surface and injecting into a reservoir all together at the same time. This categories consist of AS (alkaline-surfactant mixture), SP (surfactant-polymer mixture), and ASP (alkaline-surfactant-polymer mixture) injections.[1]

Before injecting surfactant as stand alone injection or mixing with polymer into a reservoir, detail laboratory works should be done intensively to evaluate the surfactant properties. In this papers will be discussed very detail the evaluation of the important parameters of the surfactant properties to fulfill the criteria for chemical injection. These parameters include compatibility, aqueous stability, phase behavior, interfacial tension, thermal stability, filtration, and micro-emulsion viscosity.

II. ALKALIS

To get the optimum performance of surfactant solution an alkali normally should be added in the solution. The first choice of alkali has been sodium hydroxide (caustic soda) due to its high pH value. However, in recent years sodium carbonate and sodium silicate have been and are being tested and used. The advantages of additional alkaline in the chemical solution are to generate additional reduction in IFT and to reduce the chemical adsorption by the reservoir rock. However, care must be taken when using alkaline in the injection fluid. If the reservoir brine has a high content of divalent ions such as magnesium and calcium, precipitation may occur during injection. In some cases softening the brine is required. However, if the reservoir brine is classified as high salinity and high hardness using organic alkali is suggested.[2]

III. ALCOHOLS

An alcohol is normally also added into the surfactant solution to pursue the lowest interfacial tension value. Furthermore, the addition of alcohols can reduce the optimal salinity in the solution as well; the reduction of the salinity is grater the higher the alcohol concentration. The increasing alcohol concentration also can decrease the micro-emulsion viscosity which usually is very high without additional alcohol compared to the oil viscosity.[3] Alcohols which generally mixed with surfactant are Iso Propyl Alcohol (IPA), Iso Butyl Alcohol (IBA), Iso Amyl Alcohol (IAA), and EGBE (ethyl Glycol Butyl Ether).

IV. SURFACTANTS

Surfactants are surface active agents. Their molecules compose of two different parts: a hydrophobic tail and a hydrophilic head. This leads to its interesting phase behavior. Figure 1 presents the surfactant types. In sand stone reservoirs, anionic surfactants commonly have been used, on the other hand cationic surfactants types mostly used in carbonate reservoirs.

Surfactant is usually used in EOR processes to reduce IFT between oil and water. This reduction in the tension should be sufficient to either eliminate or significantly reduce the capillary forces, which have trapped the oil in the formation. IFT measurement of surfactant injection should create ultra low interfacial tension ($<10^{-3}$ dyne/cm) to increase the displacement efficiency. The recovery of a residual oil by reduction of capillary forces depends upon the capillary number (N_c). Many experiments have proposed a number of more or less equivalent definitions of N_c. The following equation is the one that commonly used[4]:

$$N_c = \frac{\mu\upsilon}{\sigma}$$

σ = Capillary force
μ = Viscous force
υ = Shear force

The value of capillary number represents the ratio of driving force to capillary resistance force. The critical value of N_c is around 2.10^{-5}. Below this value, residual oil saturation (ROS) is relatively constant. However, above the critical value, ROS begins to decrease gradually. Basically, the relationship between capillary number and residual oil saturation should be prepared in the laboratory.

Surfactant selection for a typical reservoir environment should be based on several steps of laboratory tests. The conventional approach of surfactant selection is to screen the various commercial surfac

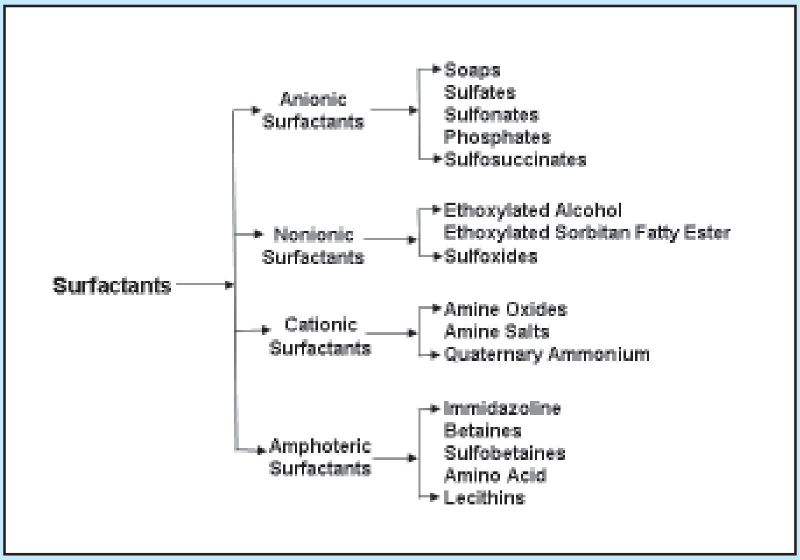

Figure 1
Surfactant Types for EOR

tants to select suitable candidate surfactants for field application. Such an approach of testing a large number of commercial surfactants is often expensive and does not ensure good performance. Another option is the concept of tailoring custom surfactant molecules for specific crude oils.

A. *Compatibility and Aqueous Stability*

A high salinity and hardness injection water generally tends to precipitate when mixture with a surfactant solution or producing incompatible fluids. Therefore, softened water will be suggested to get a better surfactant solution. The best solution to be injected into a reservoir should be a clear solution without precipitation. Some surfactants generate hazy solutions, although a clear solution is more preferable,

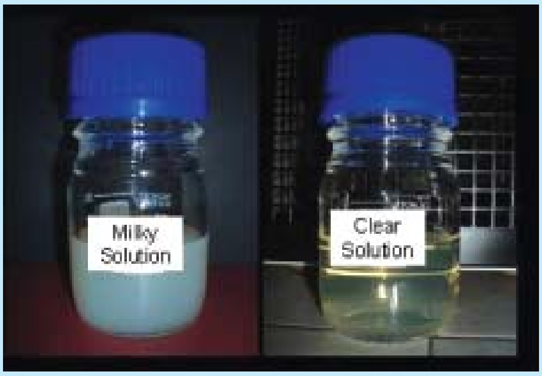

Figure 2
Comparison of milky and clear solution

Table 1
Phase behavior investigation

Hydrocarbon density	0.84	g/cc
Total surfactant conc.	0.20%	wt%
Total alcohol conc.	0.30%	wt%
WOR	1:1	
Reservoir temperature	90	Celcius
Tube size	5	mL

Na2CO3 (ppm)	Water level	Oil level	Top interface	Bottom interface	Type	Volume of oil solublized (cc)	Volume of water solublized (cc)	Oil sol. ratio (cc/cc)	Water sol. ratio (cc/cc)
0	2.98	0.88	2.98		I	0.02		0.6	
1000	3.00	0.95	2.94		I	0.06		1.5	
2000	3.00	1.15	2.90		I	0.10		2.5	
2500	3.00	1.05	2.90		I	0.10		2.5	
3000	3.05	1.00	2.90	3.75	III	0.15	0.70	3.8	17.9
3500	3.05	0.95	2.85	3.65	III	0.20	0.60	5.1	15.4
4000	3.00	0.95	2.70	3.48	III	0.30	0.48	7.5	11.9
4500	3.05	1.00	2.62	3.43	III	0.43	0.38	11.1	9.6
5000	3.05	0.95	2.52	3.35	III	0.53	0.30	13.6	7.7
5500	3.05	0.95	2.39	3.30	III	0.66	0.25	17.0	6.4
6000	3.03	0.95		3.28	II		0.25		6.3

however just because it is hazy does not mean it is not injectable. The key for deciding injectivity of hazy solution is to make sure that the solution is thermodynamically stable (equilibrated) system which will keep its micellar properties when injected. Figure 2 is the pictures of the comparison between a clear and hazy solution.

B. *Phase behavior*

Surfactant phase behavior is commonly represented using both volume fractions and ternary diagrams. Volume fraction diagrams provide an understanding of the sensitivity of the surfactant to additional electrolyte. The surfactant, cosolvent, contaminant, and cosurfactant concentration are fixed, while the concentration of electrolyte is varied. Volume fraction diagrams provide information on the electrolyte concentration at which a transition from Winsor type I to type III to type II is observed. In addition, these diagrams provide information on the solubilization of oil in the microemulsion and the optimum salinity. [5] Ternary phase diagrams represent surfactant phase behaviour as a function of varying concentrations of surfactant, oil, and water. The electrolyte concentration in the water is fixed, oil, and water is varied.

When oil is solubilized at the centre of a micelle, it is termed *Winsor type-I*; conversely, when water is solubilized at the centre of micelle, it is termed *Winsor type-II*. An intermediate bicontinuous region is termed *Winsor type-III* at which both oil and water are solubilized in a micelle. Oil solubilization parameter is the volume of oil solu

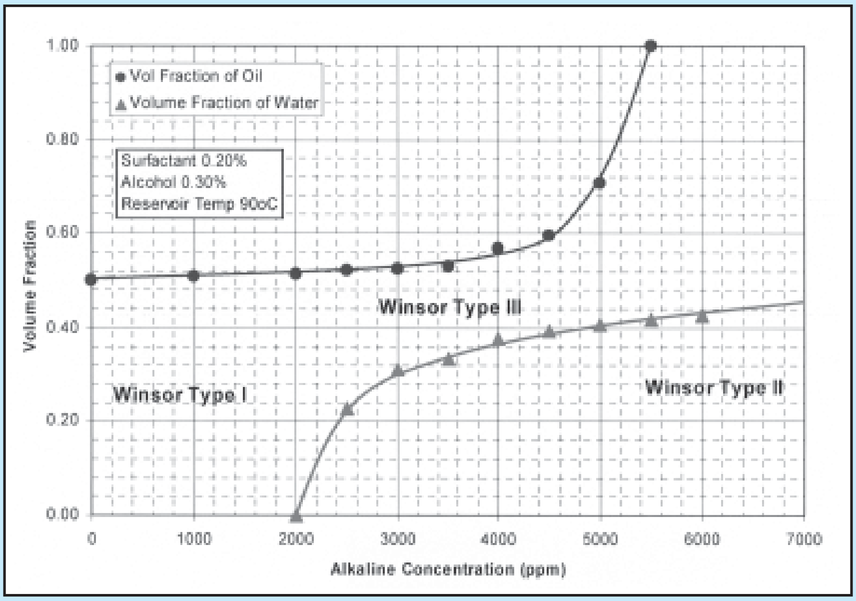

Figure 3
Volume fraction diagram

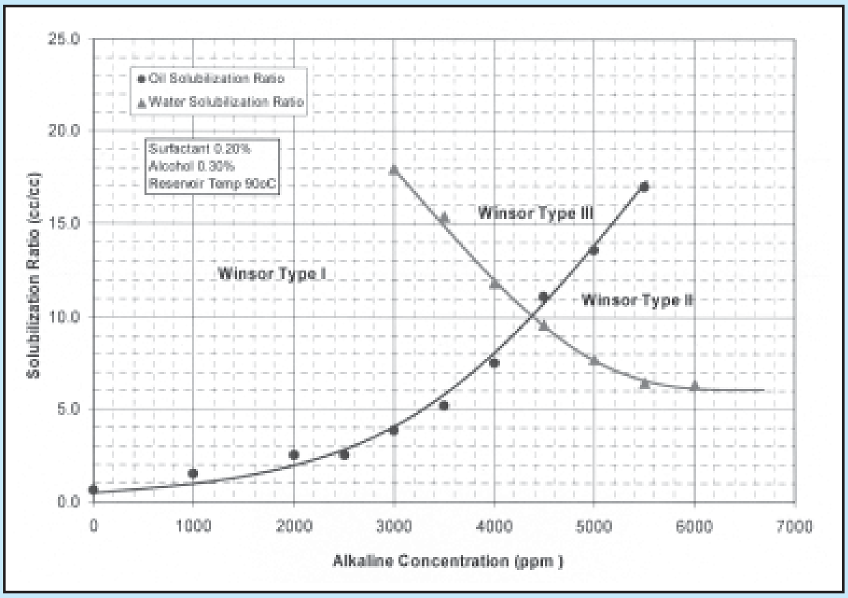

Figure 4
Solubilization ratio

Table 2
IFT Determination During Thermal Stability Test

Surfactant concentration ppm	Day-0		Day-30		Day-60		Day-90	
	Physical observation	IFT (dyne/cm)	Physical observation	IFT (dyne/cm)	Physical observation	IFT (dyne/cm)	Physical observation	IFT (dyne/cm)
250	hazy	1.15E-03	hazy	2.34E-03	hazy	4.35E-03	hazy	4.98E-03
500	hazy	6.59E-04	hazy	6.90E-04	hazy	7.13E-04	hazy	7.64E-04
1000	hazy	3.37E-04	hazy	3.97E-04	hazy	4.28E-04	hazy	4.27E-04
1500	hazy	5.69E-04	hazy	5.87E-04	hazy	6.30E-04	hazy	6.25E-04
2000	hazy	2.68E-03	hazy	2.50E-03	hazy	2.87E-03	hazy	2.92E-03

bilized per unit volume of pure surfactant, and water solubilization parameter is the volume of water solubilized per unit volume of pure surfactant. The electrolyte concentration at which equal volumes of oil and water solubilized in the microemulsion is termed optimum salinity. The phase shifts from type I to Type III and II generally occurs with increases in salinity of the brine, changing type of surfactant, type of oil, additional of alcohol, and increasing temperature. Winsor type III behavior is associated with ultra low interfacial tension and was used for EOR. However, Winsor type-I is still good for EOR as far as indicating ultra low IFT.

The procedure to determine volume fraction diagrams involves mixing 2 ml of oil with 2 ml of aqueous surfactant solution (with cosolvent whenever applicable) in a 5-ml pipette. The ends are flame-sealed to prevent loss due to volatilization. After pouring the surfactant solution, the initial oil-surfactant interface is carefully noted to obtain an accurate measurement of the actual volume of oil and aqueous surfactant solution. The pipette is mixed gently, put in the oven at reservoir temperature and allowed to equilibrate for 12 hours. The phase volumes are observed every 24 hours until equilibrium is reached. Table 1 is the reading of the micro-emulsions. The visual volume differences are used to estimate the oil and water solubilization. Figure 3 is volume fraction diagram and Figure 4 the solubilization ratio.

C. *Microemulsion viscosity*

Even though middle phase microemusion is the best condition for surfactant candidate. Measurement of microemulsion viscosity is an often neglected but crucial step for screening surfactant for field applications. High viscosities result in unacceptable high hydraulic gradients unless the flow rate is decreased. High viscosities are often an indication of unfavorable behavior such as gels or macroemulsions.[5] Adding cosolvents such as IPA will often result in low viscosity microemulsion, and also decreasing equilibration time. If a Winsor type III microemulsion has been chosen for field application, the produced oil may content high microemulsion. Therefore emulsion breaker and demulsifier may be needed for separation processes.

D. *Interfacial Tension Reduction*

Normally, middle phase microemulsion is the best solution to be injected into the reservoir. To achieve Winsor type III microemulsion high surfactant and cosurfactant should be added into the solution. If surfactant used is sulfonates based surfactant therefore the cost will be very high. To reduce the cost, basically, the lower phase or water phase is still can be injected into the reservoir as long as the optimum IFT can be achieve. Normally, to achieve Winsor type I microemulsion is needed very low surfactant concentration such as 0.1% up to 0.3%. Chun Huh correlation is normally used to estimate the IFT from the solubilization parameter, as follow:

$$\mathrm{IFT} = \frac{0.03}{(\mathrm{SPo})^2}$$

SPo is solubilization parameter of oil

E. *Thermal Stability*

Thermal stability evaluation is the most crucial work due to the long residence time of the surfactant in the reservoir, assuming that the surfactant will flow between injector and producer during 1 and 2 year time. Because of the time span and temperature any surfactant may experience degradation, broken chemical bond (thermal decomposition), and change of their properties. The direct technique to determine the thermal stability is by measuring the interfacial tension versus time. This, presumably, would measure directly the loss of the property of importance in oil recovery. Table 2 exhibits the measurement of IFT during thermal stability test.

E. *Filtration*

This test is basically to measure the capability a solution to be pumped into a reservoir and to evaluate also the possibility of surfactant "filtered" on the sand-face during injection. The work is very simple just measure volume versus time when fluid flows through a filter paper. Surfactant normally is screened using 0.22 micron filter paper. A filtration paper which has a certain pore size will help discern whether a surfactant solution has a single phase fluid or a dispersion of one phase in another. For surfactant solutions, even if the aggregated micellar structure is large, it is still small enough to go through 0.22 micron pores, even though it may not look crystal clear. So the bottom-line is really trying to determine if the fluid is a single phase, and has no phase instability for injection criteria. Filtration ratio (FR) of 1.2 normally is still tolerable. Below is the example to calculate FR:

$$FR = \frac{V_{t185} - V_{t155}}{V_{t85} - V_{t55}}$$

V = volume
t = time

V. CONCLUSIONS

Chemical flood mostly uses surfactant solution as stand alone or mixture solution with polymer to increase the oil recovery at tertiary stage. Several important parameters should be evaluated in the laboratory prior to bring into to field scale. These important parameters include:

1. The surfactant solution must be compatible with the reservoir fluids, without precipitation, single phase, and having micellar properties
2. Phase behavior indicates Winsor type III or Winsor type I with ultra low interfacial tension i.e. 10^{-3} dyne/cm are good for EOR project
3. Micro-emulsion viscosity should not too high and comparable to the oil viscosity to produce piston like displacement which alcohol may be added to reduce the viscosity
4. Thermally stable extends the time span of the residence time in the reservoir that indicated by stable IFT long time test.
5. Filtration tests are still allowable at maximum 1.2 FR

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