

THE INFLUENCE OF ALCOHOL TYPE AND CONCENTRATION ON THE PHASE BEHAVIOR AND INTERFACIAL TENSION IN OIL-SURFACTANT-COSURFACTANT-BRINE MIXTURE SYSTEM

by
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INTRODUCTION

The number of mechanism is limited for reducing the entrapment of oil in the pore space of reservoir rock and for mobilizing that residual which remains entrapped, thereby improving the microscopic displacement efficiency of a petroleum recovery process. After primary recovery by flow powered by the energy stored in the compressed fluids of reservoir, and secondary recovery by injection-pump driven water flooding, residual oil is trapped by the capillary pressure developed by interfacial tension in curved menisci between oil and water in the pore space. Figure 1.1 illustrates the interplay of capillary and viscous forces in the water flooding process. Shown in the figure is water displacing oil. The important point is that residual oil is trapped in the pore space by interfacial tension. To improve microscopic displacement efficiency is to reduce interfacial tension between oil and water.

Surfactant is surface active agent chemical that has two types of properties; lypofob (like water) and hydrofob

(like oil). The value of interfacial tension between oil and water is high, when surfactant is dissolved into water and contacts with oil, so that surfactant is not only soluble in the water, but also it is soluble in the oil. By addition of surfactant into the water and contact with oil can result in interfacial tension between oil and water from high (more less 20 - 30 dyne/cm) to lower interfacial tension (10^{-2} dyne/cm). To change the lower interfacial tension to the lowest interfacial tension conditions (10^{-4} dyne/cm), cosurfactant in oil-surfactant-brine mixture is used. Alcohols are widely used in micellar surfactant systems for enhanced petroleum recovery and are variously called cosurfactant or cosolvent. In general, alcohols modify the physico- chemical properties in ways that are important to the design of surfactant-based process for improving petroleum recovery. This research is focused on alcohol effects on oil-surfactant-brine phase behavior and interfacial tension of oil-surfactant-brine system.

II. SCOPE OF RESEARCH

Table 2.1 indicates scope of research to see the influence of types of alcohol; iso propil alcohol (IPA), iso butyl alcohol (IBA) and iso alkyl alcohol (IAA) and concentration of cosurfactant on phase behavior and interfacial tension of oil-surfactant-brine system. Type of surfactant used in this research is a liquid amphoteric surfactant. An amphoteric may contain both anionic group and nonpolar group.

III. SPECIFICATIONS

Liquid amphoteric surfactant is an easily pumpable liquid that is completely miscible with fresh water and most brines.

Activity	43 wt %
Viscosity	15.1cps
Average molecular weight	336 amu

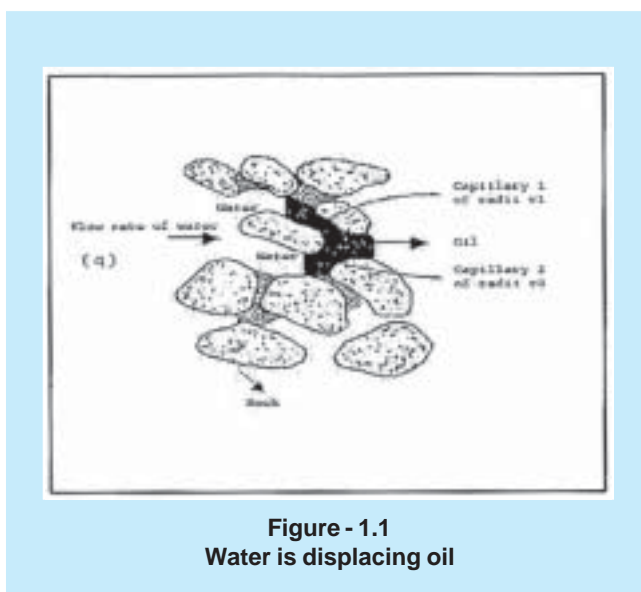


Figure - 1.1
Water is displacing oil

Insoluble	0 %
Freezing point	< 14 °F
Boiling point	100 °F
Specific gravity	1.107
pH	7.30

III. PHASE BEHAVIOR

Mixture oil-surfactant-brine can result in emulsion, which consists of three main phases; these are as follows:

- Lower phase.
 Oil-surfactant-cosurfactant-brine are mixed, then is formed lower phase, emulsion is in water phase.
- Middle phase
 Mixture of oil-surfactant cosurfactant-brine forms middle phase, which means emulsion in middle phase, called microemulsion. In this condition, the value of

interfacial tension the system of oil-surfactant-cosurfactant-brine mixture is the lowest compared to the value of interfacial tension in lower phase and upper phase.

- Upper phase
 Upper phase occurs in the system of oil-surfactant - cosurfactant-brine mixture. Emulsion exists in oil phase.

Phase-equilibrium is described in ternary diagram that contains three components: oil , surfactant and brine. Figure 3.1 indicates system of three components, surfactant, brine, oil and microemulsion.

Requirements of surfactant that can be used in enhanced oil recovery (EOR) are as follows:

- a. Low interfacial tension (IFT) between oil and microemulsion.
- b. Low interfacial tension (IFT) between water and microemulsion.

Table 2.1
Scope of interfacial and phase behavior tests

Sample No.	Mixture	Conc. Surfactant (% weight)	Typy and Conc. Of Cosurfactant/ Alcohol (% weight)		
			Iso Propyl Alcohol (IPA)	Iso Butyl Alcohol (IBA)	Iso Aryl Alcohol (IAA)
1	Oil-Water	-	-	-	-
2	Oil - surfactant - cosurfactant IPA - brine	0.100	0.00	-	-
3	Oil - surfactant - cosurfactant IPA - brine	0.100	0.10	-	-
4	Oil - surfactant - cosurfactant IPA - brine	0.100	0.20	-	-
5	Oil - surfactant - cosurfactant IPA - brine	0.100	0.30	-	-
6	Oil - surfactant - cosurfactant IPA - brine	0.100	0.40	-	-
7	Oil - surfactant - cosurfactant IPA - brine	0.075	0.10	-	-
8	Oil - surfactant - cosurfactant IPA - brine	0.100	0.10	-	-
9	Oil - surfactant - cosurfactant IPA - brine	0.125	0.10	-	-
10	Oil - surfactant - cosurfactant IPA - brine	0.150	0.10	-	-
11	Oil - surfactant - cosurfactant IBA - brine	0.075	-	0.10	-
12	Oil - surfactant - cosurfactant IBA - brine	0.100	-	0.10	-
13	Oil - surfactant - cosurfactant IBA - brine	0.125	-	0.10	-
14	Oil - surfactant - cosurfactant IBA - brine	0.150	-	0.10	-
15	Oil - surfactant - cosurfactant IAA - brine	0.075	-	-	0.10
16	Oil - surfactant - cosurfactant IAA - brine	0.100	-	-	0.10
17	Oil - surfactant - cosurfactant IAA - brine	0.125	-	-	0.10
18	Oil - surfactant - cosurfactant IAA - brine	0.150	-	-	0.10

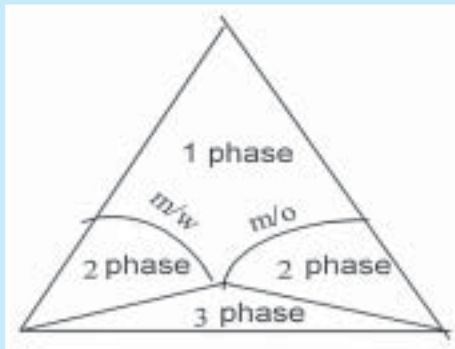


Figure 3.1
 Idealized ternary diagram for oil-surfactant-water system

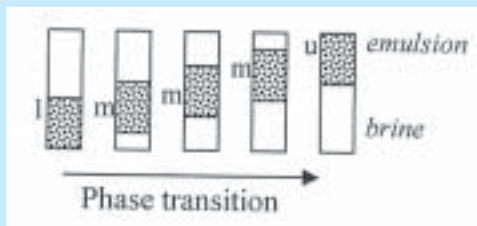


Figure 3.2
 Phase transition l, m, and u in system of oil/surfactant/alcohol/brine mixture

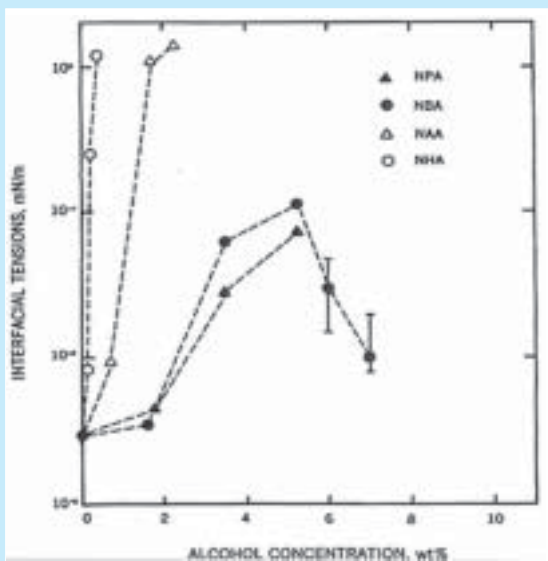


Figure 4.1
 Effect of alcohol on interfacial tension

- c. In the range of salinity limit.
- d. Stable or resistance on temperature.

Factors that influence phase transition from lower phase to middle phase and to upper phase (*l*; lower, *m*; medium and *u*, upper) in system of surfactant-oil-brine-alcohol mixture are as follows :

- a. Increasing salinity.
- b. Decreasing alkane carbon number (oil).
- c. Increasing alcohol concentration (C4, C5, C6).
- d. Decreasing temperature.
- e. Increasing surfactant concentration.
- f. Increasing brine/oil ratio.
- g. Increasing surfactant/oil ratio
- h. Increasing molecular weight of surfactant.

Phase transition from l, m, and u can be described in Figure 3.2 below.

IV. CONCENTRATION OF COSURFACTANT

To decrease the interfacial tension between oil-water, surfactant is added into oil-surfactant-water mixture, so that the value interfacial tension decreases low. Next, to get or to change the lower interfacial tension to the lowest interfacial tension, alcohol is added as cosurfactant. For example: Woodburry, N.A et al have measured interfacial tension decane vs alcohol concentration with using surfactant sodium p-(1-heptylnonyl) benzene sulfonate (SHBS) surfactant in 0.3 % (weight) NaCl solution that it is shown in Figure 4.1.

The measurement of interfacial tension between oil-surfactant-water can be determined by using Spinning Drop Interfacial Tensiometer at Laboratory that has capability to measure IFT until 10^{-4} dyne/Cm.

By using the equipment, interfacial tension oil-surfactant-water can be determined with using equation :

$$IFT = \frac{(10^6 \pi^2 \Delta \rho d^3)}{(8n^3 p^2)}$$

Where :

$\Delta \rho$ = difference of solution density

d = dropping width

p = period, msc/REv

n = refraction index

Table 5.1
 The result of interfacial tension in system of Oil - Brine Mixture

Sample No.	Concentration of surfactant (%) - weight	Concentration of cosurfactant, IPA (%) - weight	System of mixture	IFT dyne/cm	Phase behavior
S1	-	-	Oil - water	22.87	-

Table 5.2
 The influence of cosurfactant (iso propyl alcohol) on interfacial tension and phase behavior in system of oil - surfactant 0.1 % - cosurfactant IPA (0.0 - 0.4 %) - Brine (NaCl 5000 ppm) Mixture

Sample No.	Concentration of surfactant (%) - weight	Concentration of cosurfactant, IPA (%) - weight	System of mixture	IFT dyne/cm	Phase behavior
S2	0.100	0.000	Oil - surfactant - cosurfactant - brine	3.76E-04	Lower Phase Emulsion
S3	0.100	0.100	Oil - surfactant - cosurfactant - brine	2.86E-04	Lower Phase Emulsion
S4	0.100	0.200	Oil - surfactant - cosurfactant - brine	7.19E-04	Lower Phase Emulsion
S5	0.100	0.300	Oil - surfactant - cosurfactant - brine	8.42E-04	Lower Phase Emulsion
S6	0.100	0.400	Oil - surfactant - cosurfactant - brine	6.38E-04	Lower Phase Emulsion

V. THE RESULTS

Interfacial tension and phase behavior tests have been carried out based on scope of laboratory tests mentioned in Table 2.1. Section I has explained briefly that oil productivity can be improved by using water flooding method, called secondary recovery. The residual oil trapped in pore space can be displaced by surfactant flooding. The result of interfacial tension measurement between oil and water is 22.87 dyne/cm (see Table 5.1).

Next stage, Table 5.2 indicates the influence of cosurfactant on interfacial and phase behavior in the system of oil-surfactant-cosurfactant-brine mixture. Iso propyl alcohol (IPA) is the type of cosurfactant used with range of concentrations 0 – 0.4 %. Concentration of surfactant and brine solution used in the mixture are 0.1 % and 15.000 ppm. Based on the laboratory test result, concentration of cosurfactant (IPA) 0.1 % solution results in the value lowest interfacial tension (0.000286 dyne/cm) and the mixture system of forms emulsion in lower phase

or water phase (see Figure 5.1). The decrease of interfacial tension occurs drastically from 22.87 dyne / cm to 0.000286 dyne/cm. This is a prove of that surfactant and cosurfactant solutions can reduce interfacial tension between oil and water.

Table 5.3, Table 5.4 and Table 5.5 are the laboratory test results to know the influence of cosurfactant IPA (0.1 %), IBA (0.1 %) and IAA (0.1 %) solutions in the system of surfactant (0.075 – 1.5 %) –cosurfactant (0.1 %) and brine (15000 ppm) mixture. The results of phase behavior tests show lower phase emulsion at all experimental conditions. The results of interfacial tension value for each cosurfactant (IPA, IBA and IAA) with concentration of solution 0.1 % are tabulated in Table 5.6. In reality, the lowest interfacial tension values are obtained at concentration of surfactant 0.1 % solution in the system of mixture mentioned above. It can be briefly summarized that the lowest interfacial tension values are 0.000286 dyne/cm for 0.1 % IPA,

Table 5.3
 The influence of cosurfactant (iso propyl alcohol 0.1 %) on interfacial tension and phase behavior
 in the system of oil - surfactant - cosurfactant IPA (0.1 %) - Brine (NaCl 5000 ppm) Mixture

Sample No.	Concentration of surfactant (%) - weight	Concentration of cosurfactant, IPA (%) - weight	System of mixture	IFT dyne/cm	Phase behavior
S7	0.075	0.100	Oil - surfactant - cosurfactant - brine	2.33E-03	Lower Phase Emulsion
S8	0.100	0.100	Oil - surfactant - cosurfactant - brine	2.86E-04	Lower Phase Emulsion
S9	0.125	0.100	Oil - surfactant - cosurfactant - brine	1.74E-03	Lower Phase Emulsion
S10	0.150	0.100	Oil - surfactant - cosurfactant - brine	2.25E-03	Lower Phase Emulsion

Table 5.4
 The influence of cosurfactant iso butyl alcohol on interfacial and phase behavior
 in the system of oil - surfactant - cosurfactant IBA (0.1 %) - Brine (NaCl 5000 ppm) Mixture

Sample No.	Concentration of surfactant (%) - weight	Concentration of cosurfactant, IBA (%) - weight	System of mixture	IFT dyne/cm	Phase behavior
S11	0.075	0.100	Oil - surfactant - cosurfactant - brine	2.78E-03	Lower Phase Emulsion
S12	0.100	0.100	Oil - surfactant - cosurfactant - brine	6.23E-04	Lower Phase Emulsion
S13	0.125	0.100	Oil - surfactant - cosurfactant - brine	1.27E-03	Lower Phase Emulsion
S14	0.150	0.100	Oil - surfactant - cosurfactant - brine	2.23E-03	Lower Phase Emulsion

Table - 5.5
 The influence of cosurfactant iso aryl alcohol on interfacial tension and phase behavior
 in the system of oil - surfactant - cosurfactant IAA (0.1 %) - Brine (NaCl 5000 ppm) Mixture

Sample No.	Concentration of surfactant (%) - weight	Concentration of cosurfactant, IAA (%) - weight	System of mixture	IFT dyne/cm	Phase behavior
S15	0.075	0.100	Oil - surfactant - cosurfactant - brine	6.49E-03	Lower Phase Emulsion
S16	0.100	0.100	Oil - surfactant - cosurfactant - brine	4.11E-04	Lower Phase Emulsion
S17	0.125	0.100	Oil - surfactant - cosurfactant - brine	1.78E-03	Lower Phase Emulsion
S18	0.150	0.100	Oil - surfactant - cosurfactant - brine	1.94E-03	Lower Phase Emulsion

Table 5.6
 The influence of cosurfactant (IPA, IBA, IAA) on interfacial tension and phase behaviour in the system of oil - surfactant - cosurfactant 0.1 % - brine mixture

Concentration Surfactant (%)	Interfacial Tension , IFT (dyne / cm)		
	Iso Propyl Alcohol (IPA)	Iso Butyl Alcohol (IBA)	Iso Alkyl Alcohol (IAA)
0.075	2.33E-03	2.78E-03	6.49E-04
0.100	2.86E-04	6.23E-04	4.11E-04
0.125	1.74E-03	1.27E-03	1.78E-03
0.150	2.25E-03	2.23E-03	1.94E-03

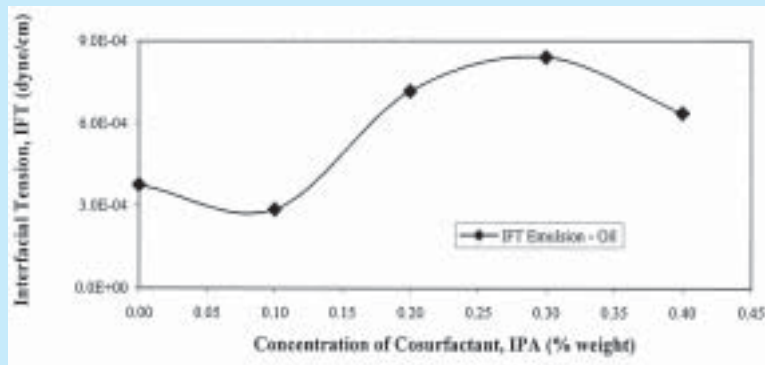


Figure 5.1
 The influence of different iso propyl alcohol concentration solution on interfacial tension and phase behavior in the system of oil - surfactant 0.1 % - cosurfactant IPA (0.0-0.4 %) - brine (NaCl 15000 ppm) mixture

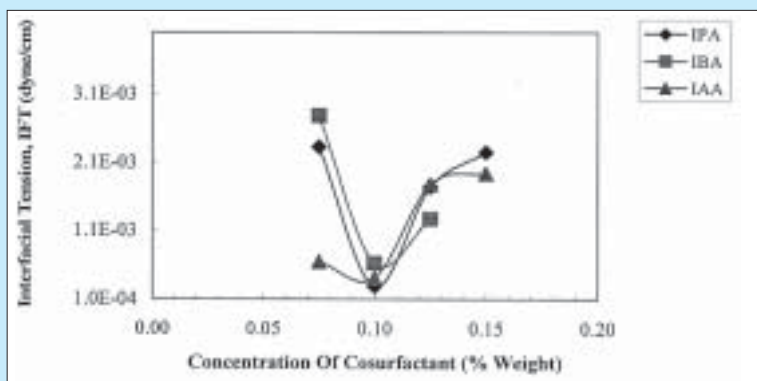


Figure 5.2
 The influence of cosurfactant (IPA, IBA, IAA) on interfacial tension and phase behaviour in the system of oil - surfactant - cosurfactant 0.1 % - brine mixture

0.000623 dyne/cm for 0.1 % IBA and 0.000411 dyne/cm for 0.1 % IAA solutions (see Table 5.6), subsequently the performance of interfacial tension curves can be seen in Figure 5.2.

VI. CONCLUSIONS

Based on the results of interfacial tension and phase behavior laboratory test can be concluded as follows :

1. Oil and water are two types of fluid that separated from each other, caused by the high interfacial tension (IFT) value (22.87 dyne/cm).
2. Alcohol type and concentration play important role in firstly, decrease of interfacial tension value from the high IFT (22.87 dyne/cm) to the lowest IFT ($X.10^{-4}$ dyne/cm) value and secondly, phase behavior in the system of oi-surfactant– cosurfactant - brine mixture.
3. In oil-surfactant 0.1 %-cosurfactant (0 - 0.4 % iso propyl alcohol, IPA)-brine NaCl (15000 ppm) mixture result in the value of lowest interfacial tension at concentration of cosurfactant IPA 0.1 %, namely 0.000286 dyne/cm.
4. Concentration of surfactant 0.1 % solution results in the lowest IFT value :
 - 0.000286 dyne/cm at 0.1 % iso propyl alcohol (IPA),
 - 0.000623 dyne/cm at 0.1 % iso butyl alcohol (IBA),
 - 0.000411 dyne/cm at 0.1 % iso aryl alcohol (IAA)
 in the system of oil - surfactant - cosurfactant – brine mixture.
5. The results of phase behavior

test show the occurrence of lower phase emulsions for all experimental conditions.

REFERENCES

1. Noronha, J.C and Shah D.O : "Ultra Low IFT, Phase Behaviour and Micro - structure in Oil/Brine/Surfactant/Alcohol Systems", Aiche Symposium Series, Vol. 78, No. 212, 1982.
2. Gardner J.E and Hayes M.E : " Spinning Drop Interfacial Tensio meter Instruction Manual ".
3. Salter, S.J " The influence of Type and Amount of Alcohol on Surfac tant -Oil - Brine Phase Behavior and Properties., SPE 6843, 1977.
4. Fayer F.J.: " Enhanced Oil Recovery", Elsevier Scientific Publishing Company, Amsterdam, Oxford, New York, 1981.
5. Adamson, A.W : "Physical Chemis- try Of Surface", Interscience Publisher, Inc. New York, 1960. •