OPEN ACCESS

International Journal of Applied Sciences and Biotechnology

A Rapid Publishing Journal

ISSN 2091-2609

Available online at:

http://www.ijasbt.org
&
http://www.nepjol.info/index.php/IJASBT/index

Indexing and Abstracting

CrossRef, Google Scholar, Global Impact Factor, Genamics, Index Copernicus, Directory of Open Access Journals, WorldCat, Electronic Journals Library (EZB), Universitätsbibliothek Leipzig, Hamburg University, UTS (University of Technology, Sydney): Library, International Society of Universal Research in Sciences (EyeSource), Journal Seeker, WZB, Socolar, BioRes, Indian Science, Jadoun Science, Jour-Informatics, Journal Directory, JournalTOCs, Academic Journals Database, Journal Quality Evaluation Report, PDOAJ, Science Central, Journal Impact Factor, NewJour, Open Science Directory, Directory of Research Journals Indexing, Open Access Library, International Impact Factor Services, SciSeek, Cabell's Directories, Scientific Indexing Services, CiteFactor, UniSA Library, InfoBase Index, Infomine, Getinfo, Open Academic Journals Index, HINARI, etc.

CODEN (Chemical Abstract Services, USA): IJASKD

Vol-2(4) December, 2014

SEM-Biotech Publishing

Impact factor*: **1.422**
Scientific Journal Impact factor#: **3.419**
Index Copernicus Value: **6.02**

*Impact factor is issued by Universal Impact Factor. Kindly note that this is not the IF of Journal Citation Report (JCR).
#Impact factor is issued by SJIF INNO SPACE.

For any type of query and/or feedback don't hesitate to email us at: editor.ijasbt@gmail.com

ISSN (Online): 2091-2609
DOI Prefix: 10.3126/ijasbt
International Journal of Applied Sciences and Biotechnology (IJASBT)

Research Article

COMPARATIVE STUDY OF AN ENHANCED OIL RECOVERY PROCESS WITH VARIOUS CHEMICALS FOR NAHARKATIYA OIL FIELD

Kalpajit Hazarika* and Subrata Borgohain Gogoi

Department of Petroleum Technology, Dibrugarh University, Dibrugarh, 786002, India

*Corresponding Author: Email: Kalpajecm44@gmail.com

Abstract

This paper reports the effect of using black liquor whose main constituent is Na- lignosulfonate, which is the effluent from Nagaon paper Mill, Jagiroad, Assam, along with Alkali and Co-surfactant in enhanced crude oil recovery from Upper Assam porous media. In this paper an attempt has been done to study the change in Inter Facial Tension (IFT) with different concentration of Surfactant and also a comparative study has been done determine the change in IFT with or without Alkali and Co-Surfactant. Increasing the surfactant concentration reduces the IFT, hence increases the recovery efficiency. Alkali changes the Wettability of reservoir rock and reduces the surfactant adsorption and also act as a in-situ surfactant production.

Keywords: Black Liquor, Na-lignosulfonate, Effluent, Alkali, Co-surfactant, Porous media, Inter Facial Tension, Enhanced Oil Recovery, Wettability, In-situ Surfactant

Introduction

The demand of oil and power has increase day by day. The reserves from where we get oil are limited. Worldwide average oil recovery rate is around 33%. Increasing this figure by 10% corresponds to an extension of the reserves of about 30 years. This constitutes a very important challenge that would leave time to enable the development of new renewable energy sources and allow an efficient energetic transition. If the reservoir energy is sufficient then no need to execute secondary recovery as well as chemical injection. But during production the reservoir energy is depleted. Due to which we go for secondary recovery as well as chemical injection. Among EOR technologies, surfactant flooding is a particularly attractive technique because one can expect an important incremental oil recovery rate related to a strong decrease of the residual oil saturation. Crude oils contain amphiphilic molecules (in particular asphaltenes and naphtenic acids), that can be in large amount in acidic or asphaltenic crudes. Depending on pH and salinity, these natural surfactants will interact with the added synthetic surfactants in order to enhance the oil recovery. It has long been an objective of the industry to develop improved processes to increase overall recovery. In light of the current higher prices and accompanying revival of interest, it seems appropriate to review understanding of, and prospects for, surfactant EOR. Adding surfactant to injected water to reduce oil/water IFT and/or alter wettability and thereby increase recovery is not a new idea. A related long-held concept for improving recovery is to generate surfactant in situ by injecting an alkaline solution which is less expensive than synthetic surfactants and converts naphthenic acids in the crude oil to soaps. (Gogoi, 2014) The other approaches to increase the recovery involved injection of a surfactant formulation made of a petroleum sulfonate and alcohol in an aqueous electrolyte solution. The main approach is the same as the previous. Key to the success of this approach were systematic studies of oil displacement leading to recognition that a dimensionless capillary number $\left[(N_C) = \frac{\mu v}{\sigma}\right]$ controlled the amount of residual oil remaining after flooding an oil-containing core at interstitial velocity v with an aqueous solution having a viscosity μ and IFT with the oil (Hirasaki *et al*., 2008). Lignosulfonate which is used as surfactant are mainly wood based chemicals manufactured from the sulfite liquor effluents of pulp and paper industries. These effluents contain sulfonated lignin, polysaccharides and wood sugar dissolved in water. The sulfonated lignin, upon purification, yields lignosulfonate products, many of which possess important surfactant and emulsion stabilizing properties. Lignosulfonate can alternatively be obtained by sulfonation of Kraft lignin. The great advantage of lignosulfonate over other commercially available sulfonate is that they are at least four times cheaper and are available in large quantities as by-product from the Canadian pulp and paper industries. This approach is competent for sustainable development of the environment.

IFT with and without Alkali

Alkali is basically used to generate in-situ surfactant. It also change the Wettability of reservoir rock and reduces the surfactant adsorption. The IFT of the system with and without alkali was measured to test the hypothesis that the soap generated by the alkali is responsible for the ultralow IFT in the presence of the colloidal-dispersion material. In the absence of alkali, the lower-phase microemulsion was homogeneous, and the ultralow IFT occurred only near the optimal salinity, as expected for conventional surfactant EOR systems. In the presence of alkali and using the protocol to ensure that a small volume of colloidal dispersion was present, a wider, ultralow IFT region was observed, especially for under optimum conditions. Apparently, this colloidal dispersion contains surface-active species which is responsible for lowering IFT between the lower-phase micro emulsion and the excess-oil phase in a manner similar to behavior of the middle-phase micro emulsion between the excess-brine and excess-oil phases. (Gogoi, 2013)

Alkaline/Surfactant Processes: Phase Behavior of Soap/Surfactant

Alkali saponifies the naphthenic acid in crude oil in situ to generate sodium naphthenate, a surfactant that helps to generate low IFT during the displacement process. Thus, an alkaline/surfactant system should be considered as a pseudo-two-surfactant approach featuring the injected surfactant and the soap. The two surfactants inject in this system will likely have different optimal salinities. The resultant salinity is somewhat different from the individuals. A mixing rule is needed to model how the optimal salinity changes with surfactant and soap concentrations. The injection of alkali is greatly dependent on the P^H of the crude oil. Alkali consumption is an important issue in sandstones because of ion exchange with clays, dissolution of silicate minerals, mixing with formation brine, and neutralization of the acids in the crude oil. Alkali consumption is also depends on minerals present in the reservoir rock. Soluble calcium minerals such as gypsum or anhydrite can contribute to alkali consumption. (Hirasaki *et al.*, 2008).

Experiment

Materials

The surfactant uses in this study is Black Liquor (BL), which is locally available waste product from paper mill (Table-1). The surfactant solutions are prepared in distilled water. The surfactant (BL) whose main constituent is Sodium (Na)-lignosulfonate ($C_{10}H_{14}N_2Na_2O_82H_2O$) with a molecular weight of 372 g/mol, a waste from Nagaon Paper Mills, Jagiroad. The region of choosing this surfactant is that it is a waste product of the mill and it is cost effective. This approach also leads to sustainable development of the environment. This Surfactant is hydrophilic because the hydrocarbon chain is less than 12 (in the lipophilic part). The other main constituents of BL are Silica in appreciable amounts, impurities such as lime, iron oxide, alumina, potash and sodium chloride and organic matter present varies and lies generally within the limit of 52-68% of the total solids in the BL. Sulfur and water content in BL are about 6 g/L and 80% respectively as done by Gravimetric analysis. Total organic solids comprise mainly lignin since the raw material of this paper mill is bamboo. The BL contains sodium salts which might also help in reducing the IFT between oil and water because it acts as an alkali. The availability of the required chemicals, which are used in this study and associated cost will also be considered in the selection. The crude oil and original water are collected from Naharkatiya fields of upper Assam basin of Oil India Limited. The oil sample and formation water will also be subjected for characterization. (Gogoi, 2013)

Table 1: List of Materials

Material	Chemical
Alkali	Sodium carbonates (Na_2CO_3) Potassium Hydroxide (KOH) Sodium Hydroxide (NaOH)
Surfactant	Black Liquor (Anionic)
Co-Surfactant	2-Propanol
Oil	Crude Oil
	Paraffin oil (Kerosene)
Formation Water	

Method

Different concentrations of surfactant solutions are prepared on the basis of volume percentage. Also the different concentration of Alkali solutions are prepared in distilled water on the basis of Molar concentration. Surface tension of different concentration of Alkali and Surfactant solutions are measured by Easy Dyne Tensimeter. The IFT of Surfactant+ Paraffin Oil (Light), Surfactant + Alkali +Paraffin Oil (Light), Surfactant + Alkali + Co-Surfactant (2-Propanol) + Paraffin Oil (Light), are measured by Easy Dyne Tensiometer. The pH of different solutions are measured by SevenMulty. The Conductivity, Salinity, Resistivity, Total dissolved solid of Formation Water and Crude Oil from Naharkatiya (OCS-5) at 22.5^{0}C is measured by SevenMulty. 2-Propanol ($CH_3CHOHCH_3$) whose density is 0.785 g/cc and molecular weight is 60.1 g/mol is used as Co-Surfactant.

Results and Discussion

Surfactant

Surfactants are very effective in reducing the IFT and create emulsion of fluids. Thus, surfactant plays an important role in Alkali-Surfactant-Polymer (ASP) flooding. Table 2 shows the specifications and properties of surfactant which is used. Ten sets of experiments have been carried out by varying the concentration of surfactant. It has been found that increase in concentration of surfactant increases the additional recovery significantly by reducing the interfacial tension, surface tension, (Babu *et al.*, 1984) mobility ratio and increases the capillary number. The main problem of surfactant is that its concentration is depleted quickly by adsorption onto the rock surface. Use of alkali reduces the surfactant depletion rate. Increase in surfactant concentration increases the additional recovery, but the rate of change is higher at lower concentration range. The main properties of the surfactant are listed in Table 2.

Table 2: Specifications and properties of surfactants (Gogoi *et al*, 2012)

Name	**Black Liquor**
Colour	Brown
Type of surfactant	Anionic
Sp. Gr at 60^0F	1.09
Density at 60^0F (g/cc)	1.09
Conductivity (5% solution in water) in(µS/cm)	4.29
Resistivity (5% solution in water) in (Ω.cm)	2.33
Salinity (5% solution in water) in(psu)	0.01
Total Solids (%)	16.3-16.7
Na_2CO_3 & Na_2O (%)	2.9
Na_2S as Na_2O (%)	0.6
NaOH as Na_2O (%)	0.363
Na_2SO_4 as Na_2O (%)	0.12
Other compound as Na_2O (%)	0.96
Total Sodium Na_2O (%)	4.65
Na-lignosulfonate (mol/lit)	0.1325

Surface Tension and Interfacial Tension of Black Liquor

The addition of surfactant decreases the IFT between crude oil and formation water, lowers the capillary forces, facilitates oil mobilization, and enhances oil recovery. The concentrations of surfactants are generally kept above their critical micelle concentration (CMC). Here in this experiment, both surface tension and IFT are determined with varying concentration of B.L. (Table 3).

Table 3: Surface Tension and Interfacial Tension of Black Liquor

S. N.	**Concentration of B.L.** (%)	**Surface tension (mN/m)**	**IFT (mN /m)**
1	1	56.8	24.2
2	2	54.2	22
3	3	54.1	20
4	4	50.2	18.9
5	5	49.6	18.6
6	6	47	18.5
7	7	46.9	18.6
8	8	46	18.3
9	9	45.7	18
10	10	44.3	17.9

The ability to lower the surface tension between aqueous solutions and other phases is one of the most significant aspects of surfactants that raise their applicability in industries (Gogoi *et al*., 2012). The CMC, one of the main parameters for surfactants, is the concentration at which the surfactant solutions begin to form micelles in large amount (Hoff *et al*., 2001).

Surface Tension and IFT of Alkali Solution

Surface tension of a system is governed by usual thermo dynamical variables and primarily by the chemical nature of the components present in the surface phase. Table 5 shows the surface tension of sodium carbonate (Na2CO3), Potassium hydroxide (KOH) and Distilled water which is used in the experiments. In our experiment, we get Surface tension of distilled water is slightly lower than standard (T = 66.71 dynes/cm). It is because, distilled water during its preparation is likely to have a small traces of grease, which lowers the surface tension value. Table 4 shows the PH of different molar concentration of sodium hydroxide (NaOH) solutions. Table 6 shows the surface tension and IFT of different concentration of (NaOH) solution. We observe that, in case of solvents NaOH and KOH, surface tension increases. It is expected, because inorganic substances (NaOH, KOH) dissolved in a liquid increases surface tension, whereas organic substance (Urea) decreases the surface tension value. The effects of alkali have been studies by varying the concentrations of alkali in the Alkali-Surfactant (AS) slug. An increase in concentration of alkali increases the additional recovery as it is well known that the injected alkali quickly reacts with the carboxylic acid groups of crude oil forming in situ surfactant.

Table 4: Surface tension of Alkali solution

S. N.	**Concentration (M)**	**Surface tension (mN/m)**		
		NaOH	**Na_2CO_3**	**KOH**
1	0.05	67.3	47.3	70
2	0.1	68.9	48	72.4
3	0.15	71.2	49.2	79.9
4	0.2	72	50.6	83
5	Distilled Water	66.71		

Table 5: P^H of Alkali solution (NaOH)

Concentration	**P^h**
0.05 M	13.717
0.1M	13.824
0.15 M	13.982
0.2 M	13.990
0.25 M	13.994

Table 6: Surface Tension and Interfacial Tension of NaOH solution

S. N.	**Concentration (M)**	**Surface tension (mN/m)**	**IFT (mN/m)**
1	0.05	67.3	22.7
2	0.1	68.9	21.3
3	0.15	71.2	21
4	0.2	71	20.8
5	0.25	71.5	18.8

Interfacial Tension of Surfactant and Alkali

The study has been carried out to get the better understanding of IFT behavior of paraffin oil with surfactant and alkali solution. The alkali solution (Ph>12) acts as a production of in-situ surfactant by reacting with acid basically Naphthenic acid present in oil. The IFT is measured by ''Easy Dyne Tensimeter''. The production of in-situ surfactant by the alkali solution and added surfactant that forms a mixed interfacial monolayer, which has the major role to decrease the IFT in between crude oil and formation water. In Table 7 we have done some IFT determination with different concentration of B.L. along with different molar concentration of NaOH solution. Here we have seen that IFT decreases with increase in surfactant concentration as well as alkali concentration. Presence of alkali in a solution significantly influences the surface tension and IFTs. Significantly lower values of interfacial tension are observed in Alkali-Surfactant (AS) system due to synergistic effect of surfactant and alkali. This reduced interfacial tension is one of the most important criteria for enhanced recovery of oil by increasing the capillary number of oil–water system. If we add co-surfactant (2-Propanol) solution with the surfactant and alkali slug it further decreases the IFT by significant value.

Table 7: Interfacial Tension of Surfactant and Alkali

S. N.	Concentration of B.L (%)	IFT (B.L.+ NaOH)				
		0.05 M	0.1 M	0.15 M	0.2 M	0.25 M
1	1	30.8	25.6	24.4	23.9	23.4
2	2	30.6	20.9	24.2	21.7	21.7
3	3	28.5	20.6	23.9	21.5	20.8
4	4	27.2	20.2	23.8	19	19.7
5	5	26.7	20.4	23.8	17.3	14.2
6	6	26.8	18.2	22.4	16.2	14
7	7	25.5	17.8	21.7	16	15.7
8	8	24.9	16.9	18.1	14.1	13.9
9	9	25.3	16.3	15.3	14.3	13.1
10	10	24.5	15.5	14.1	13.7	12.5

Table 8: IFT of Surfactant and Co-Surfactant Solution With 0.2 M Na_2CO_3 solution

S. N.	SURFACTANT (%)	IFT (Mn/m)	IFT with 2-PROPANOL
1	1	24.3	17.9
2	2	24	17.2
3	3	23.2	16.9
4	4	22.7	16.7
5	5	21.4	16.4
6	6	20.4	15.9
7	7	19.8	15.3
8	8	18.4	14.2
9	9	17.9	13.8
10	10	17.3	12.3

In Table 8 the IFT of (BL+.2M Na2CO3+2-Propanol) have been shown. The experimental values of Table 9 compare the IFT with or without co-surfactant solution. Table 10 shows the IFT of Surfactant and co-surfactant mixture.

Table 9: IFT OF B.L+ .2M KOH+ 2-Propanol

S. N.	SURFACTANT (%)	IFT (mN/m) (BL+.2MKOH)	IFT (BL+KOH+ 2-PROPANOL)
1	1	25.6	19.2
2	2	25.1	18.9
3	3	24.8	18.3
4	4	23.6	17.4
5	5	21.9	16.9
6	6	20.6	16.4
7	7	20.1	15.6
8	8	19.6	14.8
9	9	18.6	14
10	10	18.4	13.5

Table 10. IFT of different concentration of surfactant with co-surfactant solution

S.N.	SURFACTANT (%)	IFT (Mn/m)
1	1	20.9
2	2	20.4
3	3	19.9
4	4	19.5
5	5	17.8
6	6	16.2
7	7	15.6
8	8	14.8
9	9	14.3
10	10	13.9

Table 11. Specifications and properties of Naharkatiya crude oil (OCS-5)

Character	Paraffinic
API°	29
Density (g.cm-3)	0.88
Viscosity at 25°C,(cp)	9
Crude oil P^h	6.729
Conductivity (μS/ cm)	17.87
T.D.S (mg/l)	8.94
Salinity (psu)	0.02
Resistivity (Ω.cm)	5.59
Yield Point (lb/100ft^2)	2
Acid No (mg KOH/gm oil)	0.5

Table 12: Formation Water Properties of Naharkatiya (OCS-5) at 22.5^{0}C

pH	8.997
Conductivity (μS/ cm)	5.89
T.D.S (mg/l)	2.95
Salinity (psu)	3.18
Resistivity (Ω.cm)	1.7

Conclusion

When crude oil and brine are brought into contact, the acidic species naturally present in the crude oil migrate to the interface and react with the alkaline solution with higher P^h to produce interfacially active species. The IFT behavior is a function of these interfacial species concentration at the interface, which depends on their rates of adsorption and desorption from the interface. For the diluted crude oil used, the IFT first decreased when brought into contact of the alkaline solution (elongation of the crude oil drop followed by the fragmentation into smaller droplets). The IFT reduction is followed by an important increase as function of time.

Acknowledgement

The authors gratefully acknowledge the financial support provided to this project (SB/S3/CE/057/2013) from Department of Science and Technology, Government of India.

References

Babu D R, Hornof V & Neale G (1984) Use of Spent Sulfite Liquors in Enhanced Oil Recovery Operation. *J. Can. Pet. Tech*. **23** (2): 48-53. DOI: 10.2118/84-02-01

Gogoi S.B. (2013) Emulsion Flow in OIL core samples for enhanced oil recovery. *J. of Earth Science* **46**-54

Gogoi SB (2014) Effluent as Surfactant for Enhanced Oil Recovery. *J. Innovative Energy Policies*. **3**: 46-54.

Gogoi SB and Das BM (2012) Use of an effluent for enhanced oil recovery. *Indian J. of Chemical Technology* **19**: 366-370.

Hirasaki GJ, and Danhua Leslie Zhan (2005) Surface Chemistry of Oil Recovery from Fractured, Oil-Wet, Carbonate Formations,

Hirasaki GJ, Miller CA, and Maura Puerto, 3rd Dec'(2008) Recent Advances in Surfactant EOR, Event IPTC 2008. *International Petroleum Technology* Conference, PETRONAS, Malaysia.

Hoff E, Nystro¨m B, Lindman B. (2001) Polymer–surfactant interactions in dilute mixtures of a nonionic cellulose derivative and an anionic surfactant. *Langmuir* **17**(1): 28–34. DOI: 10.1021/la001175p

Horva´th-Szabo´ G, Czarnecki J, Masliyah JH (2002) Sandwich structures at oil–water interfaces under alkaline conditions. *J Colloid Interface Sci* **253**: 427–434. DOI: 10.1006/jcis.2002.8524

Nedjhioui M, Moulai-Mostefa N, Morsli A, Bensmaili A. (2005) Combiner effect of polymer/surfactant/oil/alkali on physical chemical properties. *Desalination* **185**: 543–550. DOI: 10.1016/j.desal.2005.05.013

Trabelsi S., Hutin A., Dalmazzone C, Bazin B and Langevin D. (2012) Effect of Added Surfactants on the Dynamic Interfacial Tension Behaviour of Alkaline/Diluted Heavy Crude Oil System. *Oil & Gas Science and Technology* **67**:963 – 968. DOI: 10.2516/ogst/2012033