CHARACTERISATION OF ALKALINE-ANIONIC SURFACTANT SLUGS WITH SILICA NANOPARTICLES FOR DETERMINING ULTRA-LOW IFT FOR CRUDE OIL OF UPPER ASSAM BASIN

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Abstract

Chemical flooding methods are getting significance nowadays in extracting the residual oil after conventional recovery. The paper focuses on preparing alkaline-anionic surfactant slugs along with silica nanoparticles to examine its behaviour with the crude oil sample from Upper Assam Basin for implementing in enhanced oil recovery (EOR) processes. Two common anionic surfactants (AIS) viz. Sodium Do-Decyl Sulphate (SDS) and Sodium Do-Decyl Benzene Sulphonate (SDBS) were studied based on there foam stability, aqueous stability, salinity and more specifically dynamic interfacial tension. Characterisation of the crude oil sample basically API gravity, nature of viscosity, pour point, acid number, wax and asphaltene contents; and the formation brine of that Upper Assam Basin such as alkalinity, turbidity, conductivity, pH, TDS and various ions were determined to understand its feasibility in EOR process. Main aim of this work is to observe the ultra-low IFT by preparing the surfactant slugs in addition of alkali and silica nanoparticles at different concentration level. Additionally other experiments were conducted such as effectiveness of foaming stability and aqueous stability for better reducing surface adsorption, perfect micelles concentration and for its stability in mixing condition.

Keywords: Characterisation, Anionic surfactant, IFT, foaming stability, Nanoparticles

Introduction

Chemical EOR (cEOR) is one of the most promising ways for recovering residual and leftover oil, it was not widely used in the past due to low oil prices and expensive chemical costs. However, rising oil prices and increasing demand for oil have prompted researchers to develop cost-effective cEOR technology to extract the maximum quantity of leftover oil which is trapped in the pore structure of the reservoir **[1]**. According to research, surfactant for cEOR should have the following characteristics: good thermal stability (at reservoir temperature), low retention on reservoir rock (less than 1 mg/g-rock), salt tolerance (at reservoir salinity), compatibility with the polymer/alkali used, and commercial availability at a reasonable cost and the interfacial tension (IFT) must be 10^{-2} mN/m if residual oil is to be mobilised through surfactant solution injection **[2]**. Alkali forms soaps by interacting with naturally existing organic acid in crude oil, which interacts synergistically with added surfactant to reduce surfactant adsorption, play the role of ionic strength and generate ultra-low IFT **[3].**

EOR is an alternative oil recovery method, but has downsides like chemical breakdown, high costs, and high chemical volumes. Nanotechnology offers unique qualities like wettability change, improved oil mobility, sand consolidation, and reduced interfacial IFT, but faces challenges in the petroleum sector. **[4].** They can be free or bonded together depending on attraction and repulsive factors. Nanoparticles have a higher surface-area-to-volume ratio and are highly reactive to chemicals. Similarly, nanoparticles are resistant to deterioration in high saline and temperature oil and gas reservoirs **[5].** Silica nanoparticles, which have showed promising EOR findings, are the most frequently investigated nanoparticles **[6].** Some of the key EOR processes of SiO_2 nanoparticles include disjoining pressure, injection fluid viscosity increase, asphaltene precipitation and prevention, interfacial tension, and wettability changes **[7].**

The Tipam Sandstone Formation, which dates from the Late Miocene to the Early Pliocene, is one of the most important oil-producing horizons in the Upper Assam Basin. Because of a substantial unconformity at the top, the thickness varies greatly from one location to the next. **[8].** In most mature Upper Assam Basin reservoirs, slugs with anionic surfactant/alkali EOR flooding were tried because most cEOR work has been done in sandstone formations **[9].** These mixtures lower IFT between the aqueous and oleic phases, increasing the capillary number to overcome capillary forces and boosting the reservoir's microscopic displacement efficiency.

This chapter examines the selection of anionic surfactants (AIS) for aqueous and foam-based slugs in crude oil. It considers API gravity, viscosity, pour point, asphaltene/wax content, acid number, formation brine, and ions. The best-fitting AIS EOR slug is chosen based on properties, interactions, and crude oil characterization.

Materials and Methods

Materials

Two AISs were taken under study i.e., sodium dodecyl sulphate (SDS) and Sodium Dodecyl Benzene Sulphonate (SDBS), Distilled water (DW) were procured from Department of Petroleum Engineering Laboratory, Dibrugarh University. Two crude oil samples were collected, one from Demulgaon GGS (Sample A), another from Geleki oil field (Sample B) of upper Assam Basin and formation brine of Demulgaon zone. The other chemicals used were sodium chloride (NaCl) , acetone (C_3H_6O), potassium hydroxide (KOH), deoiler, calcium carbonate ($CaCO_3$), hexane, phenolphthalein (colour indicator) and n-pentane.

Methods

Crude oil characterisation

Firstly, as both the crude oil sample contain lots of contaminants, separation was done by temperature variation, filtration process under ASTM E220, ASTM 644, ASTM E 2187-09 & ASTM F 2059. Specific gravity (SG) and API was measured using digital weighting device under standard SG method. Basic parameters were measured like amount of water contain was determined with centrifuge method (ASTM D-96). pH of the crude through potentiometer (ASTM E-70), pour point (ASTM D 97-66 & IP Designation 15/67), wax and asphaltene content (UOP 46/64), acid number through titration method (IP 186/63) and fire point by Pensky Martens Apparatus (ASTM D-93). At last, the viscous nature was measured in Anton Paar Rheometer (ASTM D445 and ASTM D7042). (Sarmah et al. 2020)

Formation Brine Characterisation

The data from formation brine characterization was used to meet analytical permitting criteria, evaluate reservoir confinement, and simulate reaction paths **[10].** Out of various options for management of produced water, mostly adopted options by the hydrocarbon exploration industries are underground injection for increasing oil recovery in the deep reservoir zone and the injection to non pay zones in the porous rocks for mere disposal purpose **[11].** PW is sometimes discharged to the surrounding environment or may be used for water flooding or reservoir pressure maintenance **[12].**

The pH was measured using a Digital Display Auto Buffer PH meter (0-14 PH range). Alkalinity was measured using a titration at room temperature with a standard acid solution. Total dissolved solids were measured using IS: 3025 methods, while total suspended solids (TSS) were measured using IS: 3025 methods. Turbidity and conductivity were determined using ASTM D 1889 standard methods, and calcium and magnesium ions were measured using complexometric titration.

Sample Preparation:

CEOR samples were prepared using weight percentage (wt%) concentration at a distilled water solution for accurate study. A magnetic stirrer was used (up to 3-6hrs) along with hot air oven to make the samples homogeneous. At certain RPM, for 1-3hrs samples were rotated in centrifuge machine for its feasibility to be applicable for stability test and for further IFT determination. The total number of samples prepared were mentioned in Table 1.

AIS/AISs Slugs Formulations

The dynamic interfacial tension between two fluids (liquid/liquid) can only be determined using the spinning drop method. This method can be used to measure low interfacial tensions ranging from 1 mN/m to 10^{-5} mN/m **[13].** So, the dynamic IFT's of two common AIS (SDBS and SDS) was determined with crude oil as the oleic phase by spinning drop tensiometer of model M6500. During the process, the oil drop was lengthened under the effect of centrifugal forces as the rotational speed of the tube increases. At high rotational speeds (greater than 2,000 RPM), gravity becomes negligible and the profile of the drop, determined by the balance between interfacial tension and centrifugal forces, takes on an elongated cylindrical shape where its length should be greater than 4 times the diameter of droplet **[14].** The modified mathematical formula applied for calculating IFT is given below:

$$IFT=1.44x10^{-7} \text{ x } (\rho_{oil} - \rho_{AIS}) \times D^3 \text{ x } RPM^2$$

Here, (ρ_{oil} – ρ_{AIS}) i.e. density difference in gm/cm^3

D = Diameter in mm.

The CMCs were obtained for these two AIS at the lowest IFTs. With that CMC of AIS, mixing was done with alkali KOH of different concentrations and detect the lowest IFT's among them. And at last different volume of silica nanoparticles were mixed with lowest IFT's of previous AIS-alkali slugs to determine the ultra low IFT. This was done to understand the behaviour of AIS/AISs with crude oil in terms of IFT reduction (Li et al. 2007).

Table 1 Showing the formulation of mixed AISs at CMC values of slugs.

AIS	**AIS Conc. in wt%**	**Alkali/ Co-surfactants**	**Alkali Conc.** in wt%	**Nanoparticles**	**NPs Conc.** in wt%	**Sample Code**
SDBS	0.2	---	----	----	----	SDBS1
	0.4		----		----	SDBS2
	0.6		----		----	SDBS3
	0.8		----		----	SDBS4
	1.0		----		----	SDBS5
SDBS	CMC - 0.6	KOH	0.2	----	----	SDBS1K1
			0.4		----	SDBS1K2
			0.6		----	SDBS1K3
			0.8		----	SDBS1K4
			1.0		----	SDBS1K5
SDBS	CMC - 0.6	KOH	CMC - 0.6	Silica NPs	0.2	SDBS1K1SNP1
					0.4	SDBS1K2SNP2
					0.6	SDBS1K3SNP3
					0.8	SDBS1K4SNP4
					1.0	SDBS1K5SNP5
SDS	0.2	---	----	----	----	SDS1
	0.4		----		----	SDS2
	0.6		----		----	SDS3
	0.8		----		----	SDS4
	1.0		----		----	SDS5
SDS	CMC - 0.6	KOH	0.2	----	----	SDS1K1
			0.4		----	SDS1K2
			0.6		----	SDS1K3
			0.8		----	SDS1K4
			1.0		----	SDS1K5

SDS	CMC - 0.6	KOH	CMC - 0.6	Silica NPs	0.2	SDS1K1SNP1
					0.4	SDS1K2SNP2
					0.6	SDS1K3SNP3
					0.8	SDS1K4SNP4
					1.0	SDS1K5SNP5

Foam stability test for AIS slugs

Foamability and foam stability are two significant properties of foam that influence its propagation during foam based EOR. Foamability is defined as the ability of the surfactants to create foam, whereas foam stability is defined as the fluctuations in foam height or volume with time after foam production **[15].** Surfactants were examined for their capacity to create stable foam and give an appropriate concentration for formulation production in the foam stability test. The initial foam volume (V_i) and time for dewatering half volume from foam ($t_{1/2}$) were observed visually after foam creation **[16].** The systems with best foaming ability exhibit the highest values of *F*q. The foaming ability coefficient (F_q) was used to quantify the foaming ability of a certain system, which was defined as **[17].**

$$F_q = \frac{3}{4}\, t_{½}\, v_i$$

Determination of Aqueous Stability of AIS

Concentrated solutions of AIS/AISs at their best reducing IFT concentration (CMC) which was determine from IFT vs. Conc. Graph and formation brine at 8640PPM reservoir salinity were combined in a glass vial, stirred, and allowed to settle for 1 hour in aqueous stability experiments. If the chemicals that make up AIS/AISs are unstable in brine at a particular salinity and temperature, they will deposit or split into various scattered phases. Aqueous stability tests establish a salinity limit beyond which all chemical components in the aqueous phase may resolute.

Results and Discussion

Crude oil characterization

The overall characterization of both the crude oil samples are illustrated in Table 2 and Table 3. This was done to understand which one is more feasibility synthetic crude for EOR process.

Table 2 Characterisation of crude oil properties of Sample A

Parameters	**Results**
SG	0.887
API (°)	26
Water Content (%)	13.57
Pour point (°C)	15

Acid Number [(mg of KOH) / (g of crude oil)]	3.93
Viscosity Nature	Pseudoplastic
Flash and Fire Point (°C)	31 & 36
Wax and Asphaltene Content (%)	2.1 & 0.0432

Table 3 Characterisation of crude oil properties of Sample B

Parameters	**Results**
SG	0.614
API (°)	36
Water Content (%)	17.85
Pour point (°C)	-5
Acid Number [(mg of KOH) / (g of crude oil)]	3.36
Viscosity Nature	Pseudoplastic
Flash and Fire Point (°C)	31 & 37
Wax and Asphaltene Content (%)	2.8 & 0.0938

Overall, the parameters like acid number which should be above 0.5 for alkali flooding were comparatively same, both showing pseudoplastic viscosity behavior, water content were high, similar flash and fire point for temperature design, wax and asphaltene content were very less i.e., lower corrosion effect and better transportation. By interpreting both the sample results on API, sample B comes under lighter crude oil section (easy to flow) compared to sample A which falls in medium crude oil, so more effectiveness for CEOR should be implemented for sample A. Also pour point of Sample B was totally below freezing point which is best suited for transportation point of view in pipelines in chilling environment. So, sample A was preferred because of its feasibility in EOR process.

Formation Brine characterization

Produced water/brine as a by-product of oil and gas production from the geologic formation, injection water, oil and salts can be mainly characterised based on salinity, about the nature of that formation. Basic characterization of formation brine is given in Table 4.

Table 4 Characterization of brine properties

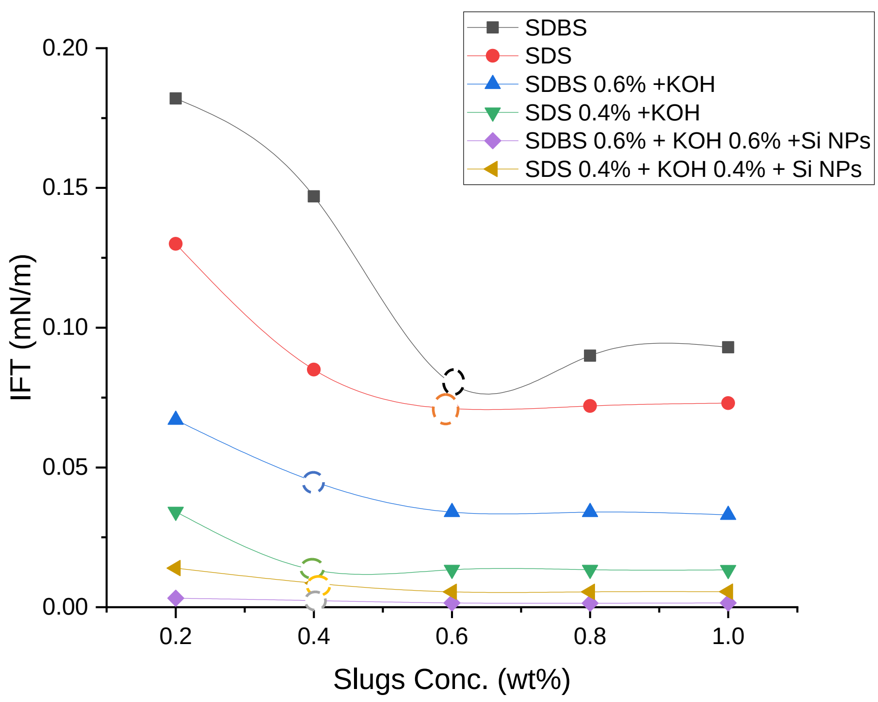
Parameters	**Results**
Conductivity (mS/cm)	14.67
Salinity (ppm)	8640
Turbidity (NTU)	170

pH	8.05
TDS (ppt)	7.76

Here, high amount of salinity indicates better resultant in caustic (alkaline) flooding as it also comes under basic form, and it is favorable for aqueous stability.

AIS/AISs slugs formulation test for Ultra Low IFT:

There was six slugs' preparation out of which from the Table 5, SDBS 0.6% + KOH 0.6% + Silica NPs were observed to be the lowest IFT (in mN/m) and for SDS at 0.4 wt% + 0.4% KOH + Silica NPs. It was seen that in addition with alkali and nanoparticles which act as a reagent in decreasing the IFT at a certain concentration for better transportation between two immiscible fluids. CMC values in the presence of crude oil can vary depending on both surfactants partitioning and the water–oil ratio, according to previous research **[18]**. In other research, sodium dodecyl sulphate anionic surfactant was employed and NPs (slightly hydrophobic and hydrophilic silica NPs) for modified EOR to better understand how surfactant and NP additions impact the IFT. The findings revealed that the critical micelle concentration (CMC) plays an important role in determining the optimal quantity of nanosuspension surfactant. Up to CMC, IFT decreases as NP-surfactant concentration rises **[19].**



Graph 1: IFT (mN/m) v/s concentration of various slugs (wt%) and determining CMC.

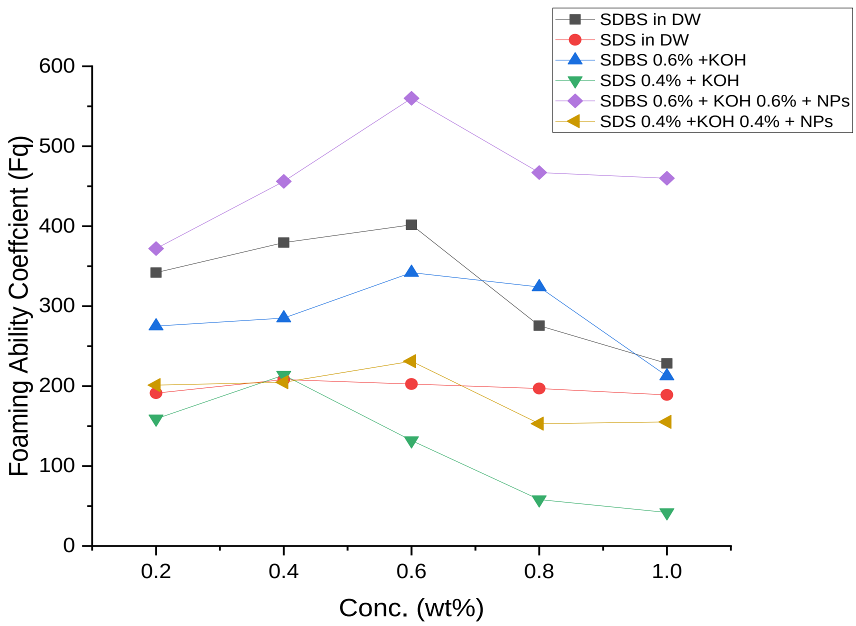
Table 5: IFT (mN/m) versus best reducing IFT of mixed AISs

Surfactant Slugs compositions	Conc (wt%)	Best reducing IFT (mN/m)
SDBS	0.6	0.08
SDBS 0.6 wt% +KOH	0.6	0.034
SDBS 0.6 wt% +KOH 0.6 wt% + Silica NPs	**0.4**	**0.0014**
SDS	0.4	0.071
SDS 0.4 wt% + KOH	0.4	0.01334
SDS 0.4 wt% + KOH 0.4 wt% + Silica NPs	**0.4**	**0.00547**

Foam Stability Test

Foamability with DW

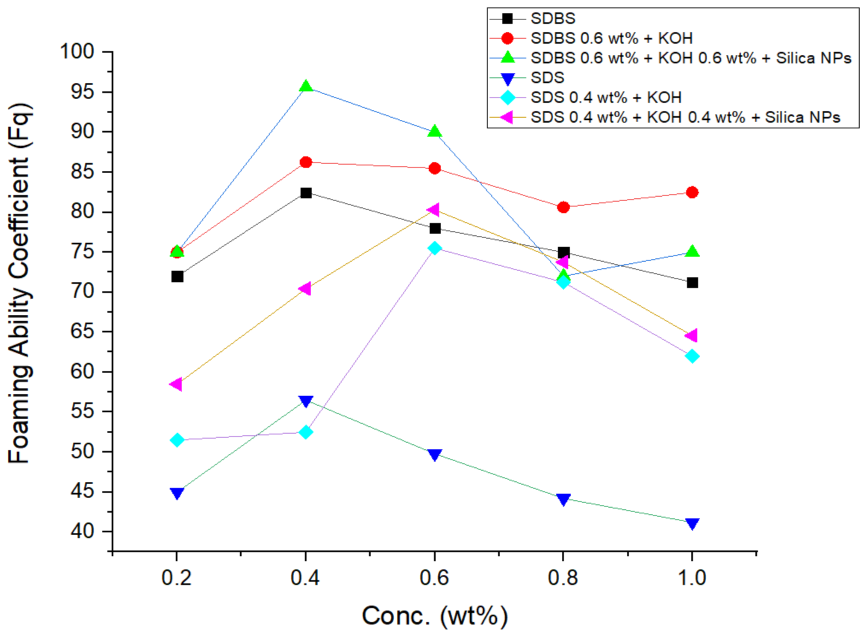
Firstly, two AISs was initially tested with distilled water for determining foaming ability. Then with the better CMC of AISs, again variable concentration of KOH was tested then by Silica NPs. In Graph 2, the foaming ability coefficients of both the surfactant slugs at different concentrations are presented. The value of F_q for a certain surfactant grew up to a certain concentration and then declined or stayed constant. The surface tension decreased as the surfactant concentration increased, resulting in enhanced foaming ability; however, beyond a specific surfactant concentration, the surface tension remained constant, therefore no further rise in foaming behaviour was seen **[20].** The concentration with the highest value of F_q was taken as its economically viable and optimum concentration limit. For SDBS, the optimum concentration was obtained at 0.6 wt% and for SDS it is 0.4 wt% after which the value of Fq decreased or remains constant with increasing surfactant concentration. By comparing the highest Fq values, the surfactants were ranked in terms of their foaming ability as SDBS>SDS with highest among was addition of KOH 0.6 wt% at 0.6 wt% of Silica NPs which act as a reagent to form better foaming stability.



Graph 2: Effect of surfactant type and concentration on foaming ability coefficient in DW along with KOH and Silica NPs

Foamability with selected crude oil sample

In this study, we had taken SDBS and SDS to investigate the effect of different surfactants with concentration in foam stability on crude oil sample. We found that SDBS has high foam stability as compared to SDS. Optimum foam stability concentration of SDBS and SDS are 0.6 wt% and 0.4 wt% respectively. By comparing highest foam stability Fq, the surfactants were ranked in terms of their foam ability as SDS>SDBS. It was noted that surfactants with smaller carbon number have smaller Fq value than surfactants with high carbon number. Foam stability of SDBS and SDS was much lower in the presence of Crude Oil, However the rank is same. The foam ability of surfactants in the presence of crude oil is rank as SDBS>SDS and optimum foam stability concentration of SDBS and SDS are 0.6 wt% and 0.4 wt% in the presence of Crude Oil.



Graph 3: Effect of surfactant type and concentration on foaming ability coefficient in crude oil along with KOH and Silica NPs

Determination of aqueous stability of the AIS/AISs

From the aqueous stability test, it was observed that all the CEOR solution at their best IFT reducing concentrations were stable at the reservoir formation brine salinity i.e., 8672PPM. There was no separation of phases in the solution while rotating it in centrifuge machine given a certain RPM. These depicts that reservoir salinity will not affect the stability of CEOR (Surfactant, Alkali) at their best reducing concentration.

Conclusion

The goal of this study is to find AISs that may be use as a brilliant, fluidized agent for EOR in the upper Assam Basin crude oil extraction. The following conclusion may be drawn from the findings:

1. Two crude oil samples were characterized with an attempt to find the most reliable one in application of EOR process. Sample A was selected in replace of Sample B for its medium viscous crude nature, perfect acid number for caustic flooding and a feasible pour point which is not below 10°C.
2. Formation Brine characterization was done to determine the nature of the reservoir. High brine salinity resultant in better CEOR implementation and perfect aqueous stability resulting in no phase change taken place between oil and different slugs' concentrations.
3. For foam stability, in addition of KOH and SNPs with both the AISs, the foaming ability coefficient was found more functional for SDBS then SDS in productivity through these slugs flooding of 0.6 wt% SDBS in addition to 0.6wt% KOH with 0.6% wt% SNPs.
4. Overall, the ultra low IFT was determined by calculating for different AIS slugs conc. and it resultant in proper effectiveness from addition of KOH and SNPs which were 0.6wt% SDBS + 0.6wt% SDS + 0.4% SNPs (CMC value) and secondly for 0.4wt% SDS + 0.4wt% KOH + 0.4wt% of SNPs. Both the mixtures will be applicable for diminishing IFT while implementing CEOR flooding in upper Assam Basin.

Declarations

Conflict of interest: Here, I confrm that there is no confict of interest.

Ethical approval: Hereby, I assure that this paper has not been previously published and the manuscript refects my own research and analysis in a truthful and complete manner.

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