Surfactant Stabilized Nanoemulsion: Characterization and Application in Enhanced Oil Recovery

Ajay Mandal, Achinta Bera

Abstract—Nanoemulsions are a class of emulsions with a droplet size in the range of 50–500 nm and have attracted a great deal of attention in recent years because it is unique characteristics. The physicochemical properties of nanoemulsion suggests that it can be successfully used to recover the residual oil which is trapped in the fine pore of reservoir rock by capillary forces after primary and secondary recovery. Oil-in-water nanoemulsion which can be formed by high-energy emulsification techniques using specific surfactants can reduce oil-water interfacial tension (IFT) by 3-4 orders of magnitude. The present work is aimed on characterization of oil-in-water nanoemulsion in terms of its phase behavior, morphological studies; interfacial energy; ability to reduce the interfacial tension and understanding the mechanisms of mobilization and displacement of entrapped oil blobs by lowering interfacial tension both at the macroscopic and microscopic level. In order to investigate the efficiency of oil-water nanoemulsion in enhanced oil recovery (EOR), experiments were performed to characterize the emulsion in terms of their physicochemical properties and size distribution of the dispersed oil droplet in water phase. Synthetic mineral oil and a series of surfactants were used to prepare oil-in-water emulsions. Characterization of emulsion shows that it follows pseudo-plastic behaviour and drop size of dispersed oil phase follows lognormal distribution. Flooding experiments were also carried out in a sandpack system to evaluate the effectiveness of the nanoemulsion as displacing fluid for enhanced oil recovery. Substantial additional recoveries (more than 25% of original oil in place) over conventional water flooding were obtained in the present investigation.

Keywords—Nanoemulsion, Characterization, Enhanced Oil Recovery, Particle Size Distribution

I. INTRODUCTION

THE conventional method of exploration and production of oil might not be able to keep up the increasing energy demands of the growing population. Therefore, the oil and gas industry is facing difficult challenges and it needs technological innovations to successfully meet the energy demands. Nanotechnology can offer some unique solutions to mitigate these challenges. Nanotechnology has the potential to transform EOR mechanism and processes. It represents the development and application of materials, methods, and devices, in which critical length scale is on the order of 1-100 nm. Proven a game changer for exploiting fossil-based fuels and, over the next 30 years, nanotechnology will be a critical component in developing fossil-based energy technologies [1].

Nanotechnology has had an immense importance in almost every industry, from consumer electronics to pharmaceuticals and telecommunication, but till now it has not been used in oil and gas exploration and production technology enormously.

New type of fluids usually called "smart fluids" can be prepared by the application of nanotechnology and this fluid has become more accessible for the oil and gas industry [2], [3]. Nanoemulsion is one of the "smart fluids" which can recover residual oil from the reservoir rocks. Nanoemulsions are a class of emulsions with a droplet size in the range of 50–500 nm and have attracted a great deal of attention in recent years because of its unique characteristics. Due to small droplet size, they are not subject to gravity-driven separation owing to the density differences of the two phases. In the year 1970, a new concept on emulsion has been developed based on the emulsion characteristics. This new class of emulsions is known as nanoemulsion and sometimes miniemulsion or ultrafine emulsion. On account of the dispersed phase droplet size, nanoemulsions are translucent or transparent, like the well known microemulsions. Emulsions and microemulsions are well known in oil and gas industry. Nanoemulsions containing oilfield chemicals may become in wide applications to well treatments (scale inhibition, fracture acidizing etc.), flow assurance (multiple additive packages), and deposit removal/clean-up. Their long-term stability and ease of preparation from a concentration precursor are compatible with oilfield logistics requirements. Emulsions are thermodynamically unstable, disperse multiphase system of two or more insoluble liquids [4] and microemulsions are isotropic, transparent or translucent, thermodynamically stable mixtures of oil and water which from spontaneously in the presence of surfactant and/or cosurfactant [5]-[7].

Stability and characteristics of nanoemulsions depend upon the preparation methodology, the order of addition of the components and the nature of the phases generated during the emulsification process and nanoemulsion do not form spontaneously [8]-[11]. Nanoemulsions, though thermodynamically unstable, can display noticeable kinetic stability. In fact, the small size of the dispersed droplets eliminates separation processes based on density difference. Due to small size of nanoemulsion droplets they favour Ostwald ripening, a mechanism by which the fluid contained in the smaller drops with highest interfacial energy is transferred to larger drops, ultimately leading to coarsening of the emulsion. For nonionic surfactants particle size distribution are influenced by HLB (Hydrophile-Lypophile Balance) values in nanoemulsion systems. The characteristics of emerging nanotechnology that attract immense interest for oil field applications include the resistance of nanoemulsions to sedimentation and creaming, which should translate to no separation in storage tanks or during transport through chemical feed lines.

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The droplet size of nanoemulsions are smaller than the pore throats in gravel packs and in reservoir matrix rock, meaning the good infectivity and penetration without filtration should be possible.

The objectives of the present study are the formation and characterization of nanoemulsion that are stable at the reservoir temperature. The formation of stable nanoemulsion using minimum amount of surfactant is the biggest challenge for its use in enhanced oil recovery. In order to investigate the efficiency of oil-water nanoemulsion in enhanced oil recovery (EOR), experiments were performed to characterize the nanoemulsion in terms of their physicochemical properties and size distribution of the dispersed oil droplet in water phase. Synthetic mineral oil and a series of surfactants were used to prepare oil-in-water emulsions. Thus, a complete study on physicochemical properties of nanoemulsion comprising of nonionic Tergitol surfactants, brine, and mineral oil have been investigated. A series of flooding experiments have been performed using the prepared nanoemulsion. The additional recoveries were calculated by material balance. Encouraging results with additional recovery more than 22% of original oil in place above the conventional water flooding have been observed.

II. EXPERIMENTAL SECTION

A. Materials

Four nonionic surfactants such as Tergitol 15-S-5 (MW=415), Tergitol 15-S-7 (MW=515), Tergitol 15-S-9 (MW=584) and Tergitol 15-S-12 (MW=738) (HLB values are 10.6, 12.1, 13.3, and 14.7 respectively) were procured from Sigma-Aldrich, Germany. All the surfactants are 99.9 % pure in nature. Mineral oil (98% pure) was used as organic phase and procured from Nice Chemicals, India. Sodium Chloride (NaCl) with 99% purity was used for preparation of brines and it was supplied by Qualigens Fine Chemical, India. The crude oil sample collected from Ahmadabad oil field was used in the flooding experiment. Reverse osmosis water from Millipore water system (Millipore SA, 67120 Molshein, France) was used for preparation of solutions.

B. Experimental Procedures

1. Determination of Critical Micelle Concentration of the surfactants

Measurement of surface tension is very much useful supplementary test method for determination of critical micelle concentration (CMC). It is particularly useful when only very small quantities of an experimental surfactant are available. In the present study surface tension of the different concentrated surfactant solutions were measured by a programmable tensiometer (Kruss GmbH, Germany, model: K20 EasyDyne) under atmospheric pressure by the Du Noüy ring method. During the measurement, the experimental temperature was maintained at 298 K. The platinum ring was thoroughly cleaned with acetone and flame-dried before each measurement. In all cases the standard deviation did not exceed ±0.1 mN/m.

2. Preparation of Nanoemulsion

Nanoemulsions were prepared by high energy emulsification method consisting of two steps.

In the first step a concentrated precursor was prepared and in the second step the amount of oil necessary to obtain the desired final concentration was added. Initially to obtain the precursor a mixture of surfactant, oil and brine was stirred using magnetic stirrer. The nanoemulsion then was prepared by adding additional oil phase to this concentrated precursor with gentle stirring.

3. Particle Size Measurement

The particle size distribution for the nanoemulsions prepared with four different nonionic surfactants was measured approximately 5 hrs after the preparation by a laser diffraction method of Zetasizer Ver. 6.00 (Malvern Instruments Ltd., Worcestershire, UK). The droplet size distribution determination was based on the best fit between the experimental measurements and the Mie theory. The software used a reflective index (RI) of 1.465 (SBO) and a dispersant RI of 1.33 (water) during the measurement. Nanoemulsions were diluted in distilled water to a droplet concentration of less than about 0.05 wt% (to eliminate multiple scattering effects), and gently stirred (to increase the homogeneity) prior to measurement. Drops of nanoemulsion were introduced into the sample presentation until the concentration reached the optimum one, indicated by the instrument. All the experiments were conducted at 25°C. Along with this, after preparation of nanoemulsions, the morphology droplets were captured by an electron microscope (Olympus, BX2 Series) and analyzed by image processing software (DP2-BSW).

4. Experimental Apparatus and Methods for Nanoemulsion Flooding

The experimental apparatus is composed of a sand pack holder, cylinders for chemical slugs and crude oil, positive displacement pump, measuring cylinders for collecting the samples. The detail of the apparatus is shown in Fig 1. The displacement pump is one set of Teledyne Isco syringe pump. Control and measuring system is composed of different pressure transducers and a computer. The physical model is homogeneous sand packing model vertically positive rhythm. The model geometry size is $L= 35$ cm and $r= 3.5$ cm. Sandpack flood tests were employed for the evaluation of the effectiveness of microemulsion flooding. For uniform sandpacks, 60−70 mesh sand was poured in to the coreholder which was vertically mounted on a vibrator and filled with corresponding brines for different floodings. The coreholder was fully filled at a time and was vibrated for one hour. The wetpacked sandpack was flooded with the heavy oil until water production ceased (water cut was less than 1%). The initial water saturation was determined on the basis of mass balance. The wetpacked sandpack was flooded with the Crude oil at 400 psig to irreducible water saturation. The initial water saturation was determined on the basis of mass balance. Waterflooding was conducted horizontally at a constant injection flow rate. The same injection flow rate was used for all the displacement tests of this study. After water flooding, ~0.5 PV nanoemulsion slug was injected followed by ~2.0 PV water injection as chase water flooding.

The same methods are followed for different nanoemulsion systems at various salinities.

The effective permeability to oil (k_o) and effective permeability to water (k_w) were measured at irreducible water saturation (S_{wi}) and residual oil saturation (S_{or}), respectively, using Darcy's law equation. The permeability of the sand packs was assessed with the Darcy equation, Eq. (1), used with fluid flow in porous materials. For a horizontal linear system, flow rate is related with permeability as follow:

$$q = \frac{kA}{\mu}\frac{dp}{dx} \tag{1}$$

where, q is volumetric flow rate (cm^3/sec.), A is total cross-sectional area of the sand pack (cm^2), μ is the fluid viscosity (CP), $\frac{dp}{dx}$ is the pressure gradient (atm/cm) and k is Permeability in Darcy.
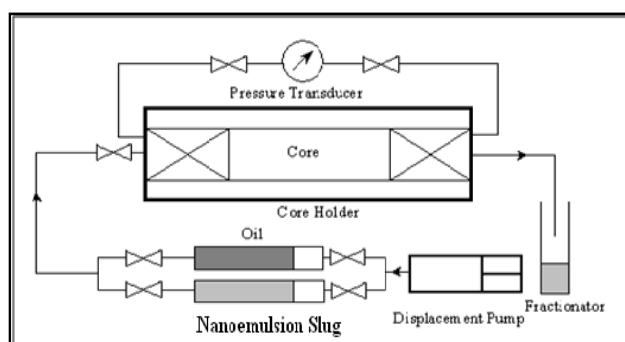

Fig. 1 Schematic diagram of experimental set-up for Nanoemulsion Flooding in sandpacks

5. Calculation of Oil Recovery by Nanoemulsion Flooding

The recovery factor was calculated by two methods, either using a secondary oil displacement procedure or by means of a tertiary oil displacement technique, overall comprising two steps:

(a) The first step, corresponding to the secondary recovery method, involves the injection of brine into the sand pack, as described in the procedure above. At this point, a certain amount of oil is recovered and another remains in the sand pack. The brine only pushes away the oil found in the sand pack, under high interfacial tensions and lacking any chemical interaction. The amount recovered is calculated via a mass balance,

Volume of oil remaining in the sand pack = Volume (oil injected) – Volume (oil expelled) and

(b)The second step is performed with the objective of recovering any amount of oil still stored in the sand pack, which corresponds to the implementation of a tertiary recovery method, whereby microemulsion is injected in the fourth step of the process. This solution works by reducing interfacial tensions between the contacting fluids and, as a result, the volume of recovered oil increases.

The recovery factor is obtained by summing up the amounts of oil recovered in each step (secondary and tertiary oil displacement process) and is expressed in percentage (%)

$RF_{Total} = RF_{SM} + RF_{TM}$

where, RF_{Total} = Total recovery factor (%), RF_{SM} = Recovery factor obtained by secondary method (%), RF_{TM} = Recovery factor obtained by tertiary method (%).

III. RESULTS AND DISCUSSION

A. Critical Micelle Concentration of the surfactants

It is well known that the surfactants reduce the surface tension of water by getting adsorbed on the liquid–gas interface. The critical micelle concentration (CMC), one of the main parameters for surfactants, is the concentration at which surfactant solutions begin to form micelles in large amount [12]. Surface tensions of the above three surfactants (Tergitol 15-S-5, Tergitol 15-S-7, Tergitol 15-S-9, and Tergitol 15-S-12) solutions at different concentrations were measured and plotted as a function of concentration in Fig. 2. The concentration at the inflexion point of the curve is critical micelle concentration. For ethoxylated nonionic surfactant CMC increases with increase in EON [13]. In the present study same result has been also found in case of the employed nonionic surfactants that with increasing EON, the CMC value of the surfactant increases. The CMCs values for the surfactants with EON 5, 7, 9, and 12 are 0.002, 0.0031, .0042 and 0.0051 wt% respectively.
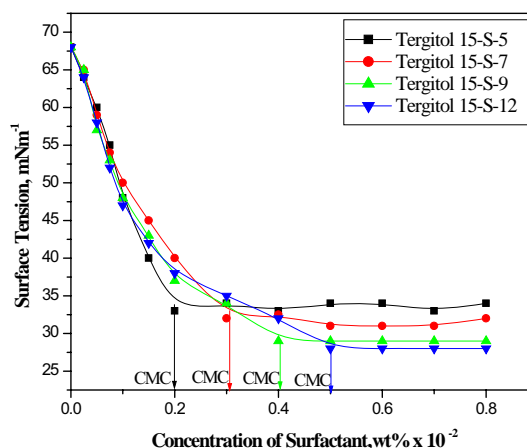

Fig. 2 Surface tension of the used surfactants with variation of their concentration and CMC calculation

B. Particle size distribution

The nanoemulsification method developed makes use of a series of nonionic ethoxylated surfactants. To obtain kinetically stable nanoemulsion, with a small droplet radius, the emulsification path is very essential. Generally all nonionic surfactants are assigned with a HLB number, an empirical value that defines the hydrophile/lypophile character of the surfactant in order to provide the best match with a given oil to produce the maximum stability of an emulsion [14]. Particle size distributions in nanoemulsions at 2 wt% NaCl solutions for four nonionic surfactants such as Tergitol 15-S-5, Tergitol 15-S-7, Tergitol 15-S-9, and Tergitol 15-S-12 are shown in Fig. 3. The mean particle diameter and polydispersity index (PDI) have been calculated from intensity, mass and number bimodal distribution.

However, in each case only % intensity vs. particle size distribution curves has been shown for clarity. Usually size effects are due to significant colloidal interaction between particles, that is to say when the particles are considerably smaller than 10 nm. Two different factors are acting behind the droplet size distribution: firstly the particle deformability decreases with droplet size and secondly the width of the droplet size distribution usually also decreases with droplet size. In case of low HLB value (10.6), nanoemulsion shows the Z-average diameter of 429.456 nm which is greater than that of nanoemulsions with high HLB values (Z-average diameters are 305.607 nm, 226.582 nm, and 22.812 nm for HLB values of 12.1, 13.3, and 14.7 respectively). The Z-average diameter is the mean hydrodynamic diameter and is calculated according to the International Standard on dynamic light scattering ISO13321. The Z-average diameter is intensity weighted and is therefore sensitive to the presence of large particles. It is a suitable parameter for following processes such as particle aggregation or crystallization. Dependence of particle size on HLB provides flexibility to formulation of nanoemulsions. The results of the particle size analysis of the nonionic surfactants have been shown in Table 1. As HLB values of nonionic surfactants increases Z-average diameter decreases. In case of the employed nonionic ethoxylated surfactants as HLB value increases ethylene oxide number (EON) also increases. Therefore activity of the surfactant also increases and the nanoemulsion particle size is influenced to reduce and offering smaller particle size distribution with increasing HLB values. The nanoemulsion photographs have been shown in Fig. 4. In Fig. 5 a relationship between HLB values of surfactant and Z-average diameter of the particle has been shown. The electron microscopic image of Tergitol 15-S-7 nanoemulsion has been shown in Fig. 6.
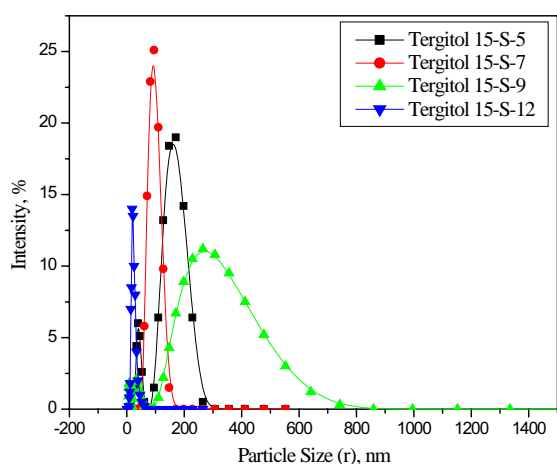
Fig. 3 Particle size distribution for nanoemulsion composed with different nonionic surfactants

TABLE I
RESULTS OF THE PARTICLE SIZE MEASUREMENTS OF THE NANOEMULSIONS

Sample Name	Z-Average diameter (nm)	PDI	Intercept	Peak Vol. % r.nm
Tergitol 15-S-5	429.456	0.498	0.908	14.44
Tergitol 15-S-7	305.607	0.387	0.949	50.00
Tergitol 15-S-9	226.582	0.755	0.958	43.21
Tergitol 15-S-12	22.812	0.538	0.957	49.59

Fig. 4 Photographs of prepared nanoemulsions with Tergitol 15-S-5, Tergitol 15-S-7, Tergitol 15-S-9 and Tergitol 15-S-12 (From left to right)
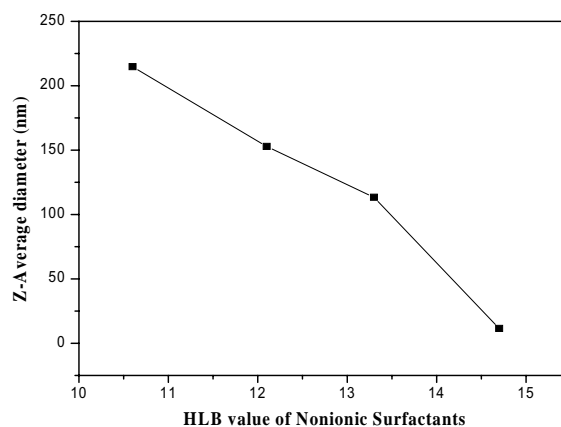
Fig. 5 Relation between Z-average diameters (nm) vs. HLB values of nonionic surfactants

Fig. 6 Microscopic images of nanoemulsions prepared with surfactants (a) Tergitol 15-S-9

C. Nanoemulsion Flooding and Recovery

The sand pack was flooded with nanoemulsion slug after water flooding and the Fig. 7 shows the oil recovered with pore volume injected into sand pack. The figure of waterflood oil recovery shows an early breakthrough and channel flow which caused much lower oil recovery. During injection of nanoemulsion slug, water-cut declines gradually, and then again reaches 100 % at the end of flooding. After the injection of nanoemulsion slug, the trapped oil droplets or ganglions are mobilized due to a reduction in interfacial tension between oil and water. The coalescence of these drops leads to a local increase in oil saturation. Behind the oil bank, the surfactant now prevents the mobilized oil from being retrapped.

The effectiveness of the nanoemulsion at different brine concentration on enhanced oil recovery was tested with three sets of flooding experiments performed in the sandpack systems. In the present work, the experiments were carried out in sand pack, the water flood recovers almost 50% of the original oil in place (OOIP) because of higher porosity (~37%) and permeability. During water flooding, as the water cut reaches above 95%, it was subsequently flooded with nanoemulsion slugs, followed by chase water. The recovery of oil and water cut with pore volume (PV) injected for three different nanoemulsion systems is presented in Fig. 7. It has been found that water begins to break through when the injected volume of water reaches 0.15 PV, and then water cut sharply increases above 90% for each case. During injection of nanoemulsion slug, the water cut declines gradually and then reaches 100% at the end of flooding. Fig. 7 also shows that the cumulative oil recovery by nanoemulsion flooding is higher in the case of nanoemulsion prepared with Tergitol 15-S-12 on because of significant physicochemical properties of nanoemulsion in case of that surfactant.

The small droplet size of the nanoemulsion can help it to penetrate into pore throats in gravel packs and in reservoir matrix rock. Therefore, mobilization of oil in pore throats would be easier and consequently recovery efficiency increases. The mechanism results in a reduced water mobility that improves both vertical and areal sweep efficiency. The additional recovery of oil over water flooding is 22.62, 22.90, and 23.30 % when the nanoemulsion slugs with Tergitol 15-S-7, Tergitol 15-S-9, and Tergitol 15-S-12 were used respectively. However, the proper design of the nanoemulsion slug should be performed by feasibility analysis, considering the operating costs and market value of the crude.
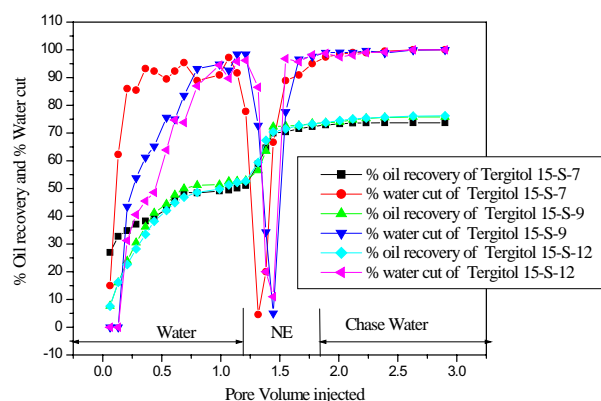

Fig. 7 Production performance of Nanoemulsion (NE) flooding for different surfactants

TABLE I
POROUS MEDIA PROPERTY AND OIL RECOVERY BY NANOEMULSION FLOODING

Expt. No. & Surfactants used	Porosity	Permeability, k (Darcy)		Design of chemical slug for flooding	Recovery of oil after water flooding at 95% water cut (%OOIP)	Additional recovery (% OOIP)	Saturation, % PV		
		k_w (S_w=1)	k_o (S_{wi})				S_{wi}	S_{oi}	S_{or}
1 (Tergitol 15-S-7)	38.665	4.837	0.032	0.5PV Nanoemulsion + Chase water	50.71	22.62	18.52	80.9	18.7
2 (Tergitol 15-S-9)	38.665	4.669	0.028	0.5 PV Nanoemulsion + Chase water	51.62	22.90	17.50	82.5	20.4
3 (Tergitol 15-S-12)	39.586	4.449	0.025	0.5 PV Nanoemulsion + Chase water	51.5	23.30	17.28	85.7	20.2

IV. CONCLUSION

In order to investigate the efficiency of oil-water nanoemulsion in enhanced oil recovery (EOR), experiments were performed to characterize the nanoemulsion in terms of their physicochemical properties and particle size distribution of the dispersed oil droplet in water phase. As Eon of the nonionic surfactants increases CMC values of the surfactants also increases. From the experimental results a new correlation between HLB of surfactant and particle size distribution has been established.

With increasing HLB values of nonionic surfactants Z-average diameter of the nanoemulsion decreases due to higher activity of the nonionic surfactant with higher HLB value and EON. Encouraging results with additional recovery more than 22% of original oil in place above the conventional water flooding have been observed. Recovery is also high in case of higher HLB surfactant nanoemulsion.

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