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Synthesis and Characterization of Triethanolamine Derivative of Sodium Dodecy l Sulphate and its Use in Enhanced Oil Recovery

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ABSTRACT

The paper deals with the synthesis and characterization of a new surfactant and its use in Alkali-Surfactant-Polymer (ASP) flooding in enhanced oil recovery (EOR). The material has been synthesized from sodium dodecyl sulphate and triethanolamine. The synthesized surfactant has been characterized by measuring the surface tension of its aqueous solution and it has been found that the surface tension of derivative surfactant is much lower than that of pure surfactant. The developed surfactant has been used for ASP flooding and substantial additional recovery has been observed after conventional water flooding.

Keywords: *SDS, Derivatives, Triehanolamine, ASP, Flooding, EOR*

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INTRODUCTION

The displacement efficiency in the enhanced oil recovery (EOR) is related to capillary number (N_c) because of its effect on residual oil saturation. The residual oil trapped in the reservoir pore structure could be displaced when the value of N_c increases. An effective way to enhance N_c can be achieved by reducing the oil/water interfacial tension and improving the fluidity of displacement liquid. Nowadays, a dilute aqueous solution of surfactant and polymer solutions is used in EOR [1, 2]. The most widely used water-soluble surfactant and polymers used are sodium dodecyl sulfate (SDS) and partially hydrolyzed polyacrylamide (PHPAM) in chemical flooding [3, 4]. Surfactant and polymer slugs in chemical flooding system not only produce an ultra-low interfacial tension but also a high apparent viscosity, so they can improve both displacement efficiency and sweep efficiency. Thus, the ultimate recovery can be enhanced greatly [5].

At the beginning of the new century, a shift in emphasis in chemistry was apparent with the desire to develop environmentally benign routes to myriad materials using non-toxic reagents, solvents, and catalysts [6]. Recently, “ideal synthesis” was defined as one in which the target compound is generated in one step, in quantitative yield, from readily available and inexpensive starting materials in a resource-effective and environmentally acceptable process [7]. Recently, organic reactions in water without use of harmful organic solvents have attracted much attention, because water is a cheap, safe, and environmentally benign solvent [8–10].

Extended surfactants are amphiphiles containing a spacer arm with intermediate polarity between tail and head groups [11–13]. This spacer arm plays the role of the so-called lipophilic linker [14–16], and seems to be a handy way to improve solubilization in microemulsions [12, 17] and to lower the surface or interfacial tension [18], particularly with long alkanes and polar oils because it promotes an extended thickness of the interfacial zone [19, 20]. Extended surfactants have been synthesized so far with a linear or branched alkyl tail, a polypropylene oxide chain spacer from 4 to 14 propylene oxide units, and different kinds of polar groups, e.g., sulfate, carboxylate, ethoxylate, glycosides, and their combinations [21–25]. Sulfate head group extended surfactants have been found to exhibit the typical features of so-called optimum formulation, i.e., minimum surface or interfacial tension in the proper physicochemical conditions [12, 26–28].

This work presents the synthesis of a triethanolamine derivative of SDS. In this compound, hydrophilic moieties are connected as a triethanolamine group. The physicochemical properties, such as surface tension, conductance, and critical micelle concentration (CMC) of this compound and also their use in enhanced oil recovery have been studied. We have also compared the oil recovery of crude oil from the reservoir by using SDS as well as its derivative as a surfactant.

THEORY

When a surfactant is added to an oil-water mixture, the hydrophilic head group of the surfactant prefers to aggregate in solutions at the interface and the hydrophobic tail group remains in the oil phase. Therefore, the interfacial tension between oil-water interfaces decreases significantly and is more favorable in the enhanced oil recovery. In the present study, the triethanolamine derivative of SDS was synthesized. Presently synthesized surfactant contains three -OH groups at the head; hence, it is more polar in nature than pure SDS and hence its surfactant character is better than that of pure SDS. The schematic diagram of the triethanolamine derivative of SDS orientation between oil and water is shown in Figure 1. The aberrant behavior of surfactant is attributed to molecular structure and aggregation behavior with water. At the interface, the long alkyl chain extends into oil and the polar head group lays on water.

EXPERIMENTAL

Material Used

Anionic surfactant, SDS (~99% purity), was used for the present study. SDS ($C_{12}H_{24}SO_4Na$, M.W. D 288.38) was purchased from Central Drug House (P) Ltd., India. The triethanolamine (TEA) and reagent grade

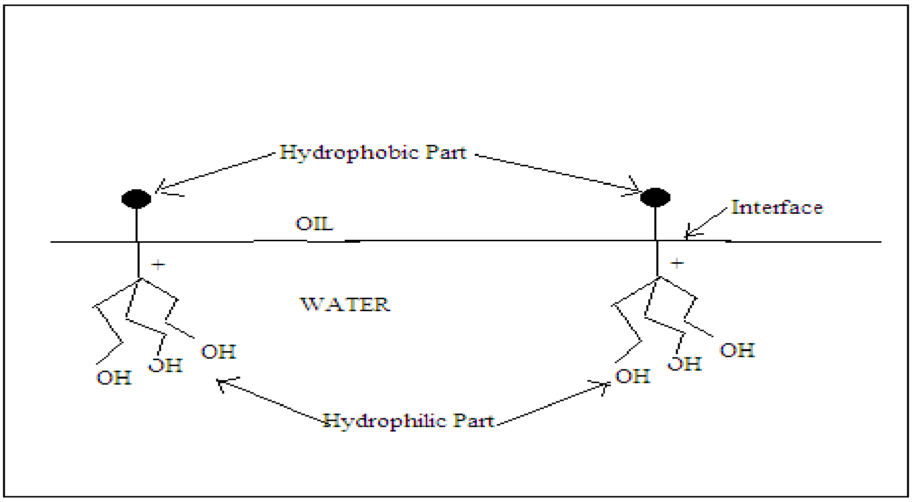

Fig. 1 Schematic Diagram of SDS Derivative Interaction with Oil and Water.

sodium hydroxide (96% purity) were purchased from S. D. Fine-Chem Ltd., India. PHPAM (Polymer Pusher 1000, SNF Floerger, France) was used as the polymer. The crude oil used in the flooding experiments was collected from Ahmadabad Oil field (India). It was degassed and dehydrated. The physical properties of crude oil are as follows: (i) viscosity: 50.12 mPa.s at 45ºC, (ii) total acid number: 0.038 mg KOH/g, (iii) API gravity: 38.5 (iv) Color: Blackish.

Experimental Method for Synthesis of SDS Derivative

Triethanolamine (0.5 mole) was dissolved in benzene and poured into a 2 L two-necked, round-bottomed flask. A condenser was fixed at one neck and Lauryl sulfuric acid dissolved in benzene was added slowly through the other neck of the flask while maintaining uniform stirring. The whole assembly was partially immersed in cold water (~10ºC) while the neutralization process continued. When the neutralization was complete, the content of the flask was poured into 2 L single-necked round-bottomed flask and the benzene was distilled off. Subsequently, the prepared material was used as such. The reaction scheme of the synthesis is shown below in Figure 2.

Measurement of Surface Tension of Surfactant Solutions

Surface tension measurements were carried out using an Autotentiometer (Model: 6801ES with platinum ring) under atmospheric pressure by the ring method [29]. The ring method is based on the fact that any enlargement of a phase boundary area between liquid/air and liquid/liquid can take place only after overcoming some resistance. This resistance is proportional to existing surface

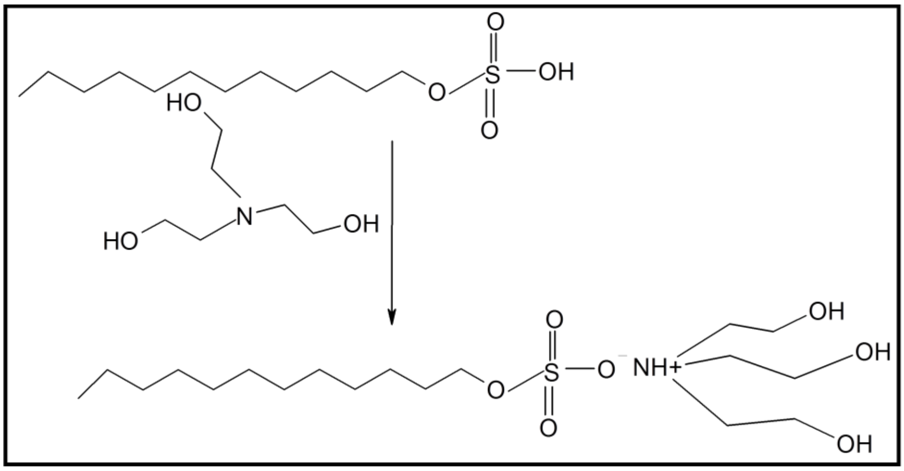

Fig. 2 Reaction Scheme of Synthesis of SDS Derivative.

and interfacial tension and the result can be directly read in mN/m with an accuracy of ±0.1 mN/m. The platinum ring was thoroughly cleaned and flame-dried before each measurement. To determine the surface tension, the vertically hung ring was dipped into the liquid and then subsequently pulled out. The maximum force required to pull the ring through the interface was taken as the surface tension, γ (mN/m). The tensiometer was calibrated with pure water at 298 K. The reported values of the surface tension are average values of at least three measurements.

Flooding Test

The experimental set-up (Fig. 3) for sand pack flooding tests consists of four components, a sand pack holder, a displacement pump (Teledyne Isco), cylinders for holding crude oil, and chemical slug and fraction collectors. The detailed experimental methods for flooding test have been introduced in the literature [30]. In all the flooding experiments ~0.3PV ASP slug was injected followed by ~0.2 PV polymer buffer and chase water.

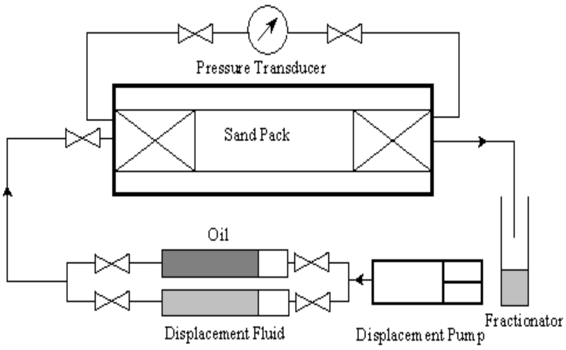

Fig. 3 Schematic Diagram of Crude Oil Flooding System.

Results and Discussion

Surface Tension of ASP Slugs and Surfactants

Surface tensions of synthesized triethanolamine derivative of SDS at different concentrations were measured and compared with pure SDS as shown in Figure 4. In both cases, the surface tension decreases with increase in concentration of surfactants up to critical micelle concentration (CMC). However, at the same concentration, the surface tension of triethanolamine derivative of SDS is much lower than that of SDS. The CMC of SDS derivative (0.0156 wt.%) is also much lower than that of pure SDS (0.1 wt.%). As the objective of the study to use the synthesized surfactant for ASP flooding system, the interaction of surfactant with alkali and polymer has also been characterized by measurement of surface tension of the system as shown in Figure 5. From the figure, it may be seen that polymer increases the surface tension of the surfactant solution due to interaction of the functional group of both polymer and ionic surfactant [31–33]. On the other hand, addition of alkali reduces the surface tension as alkali itself reduces the surfactant of the water significantly [34, 35]. The effects of interactions between alkali and surfactant with polymer viscosity must be considered while injecting such ASP slug for enhanced oil recovery.

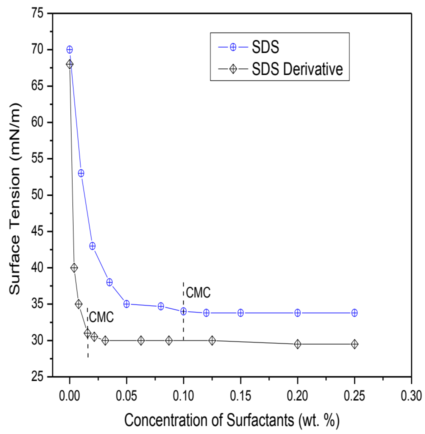

Fig. 4 Surface Tension of SDS and its Triethanolamine Derivative at 25°C.

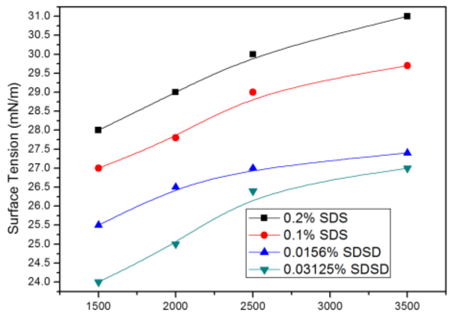

Fig. 5 Surface Tension Measurement of Different ASP Slug (0.7% NaOH) with Varying Polymer Concentrations at 25°C.

Use of SDS and Synthesized SDS Derivative in EOR

A series of experiments have been performed using ASP slugs having different compositions. A comparative study has been made using SDS and triethanolamine derivative of SDS as surfactant. As discussed earlier, polymer controls the mobility, alkali forms in-situ surfactant and alters wettability, and surfactant reduces the interfacial tension to an ultra-low value. Typical results are shown in Figure 6. Alkali and polymer concentration were taken as 0.7% NaOH and 2000 ppm PHPAM. It was found that the additional recovery was higher when synthesized triethanolamine derivative of SDS was used as surfactant even at very low concentrations (0.0156 and 0.0078%) compared to pure SDS (0.1%). A comparative picture of the cumulative oil recovery is shown in Figure 7. A summary of the displacement results and oil recovery are shown Table I. So the additional oil recovery by ASP flooding using pure SDS in ASP slug is ~24.5% for 0.1% SDS whereas around 30% OOIP over conventional water flooding were obtained at 0.0078 and 0.0156% of triethanolamine derivative solutions in ASP slug.

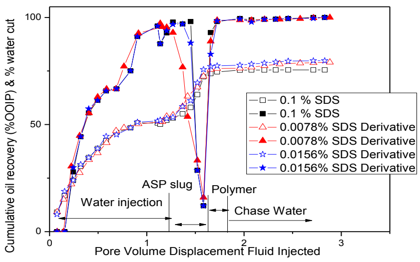

Fig. 6 Production Performance of Alkali-Surfactant-Polymer Flooding (where X 2000 ppm PHPAM and 0.7wt% NaOH used).

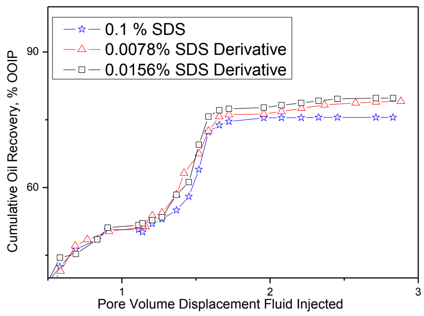

Fig. 7 Comparison of Cumulative Oil Recovery by ASP Flooding (2000 ppm PHPAM and 0.7 wt % NaOH).

CONCLUSIONS

In the present study, an attempt has been made to modify the hydrophilic nature of SDS and its applicability in enhanced oil recovery by preparing its triethanolamine derivative. Its interfacial properties for chemical flooding are very attractive for enhanced oil recovery. Experimental results show that flooding with ASP slug using SDS derivative gives additional oil recovery ~30% using a very small concentration of surfactant whereas ~24.5% additional recovery has been observed with pure SDS even with more than ten times higher concentration of SDS.

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NOMENCLATURE

ASP Alkaline-surfactant-polymer
CMC Critical micelle concentration
OOIP Original oil in place
SDS Sodium Dodecyl Sulphate
SDSD Triethanolamine Derivative of Sodium Dodecyl Sulphate
k_o Effective permeability to oil, Darcy
k_w Effective permeability to water, Darcy
N_c Capillary number
R Recovery factor
S_o Oil saturation after the injection of each solution
S_{or} Residual oil saturation
S_{rj} The residual saturation for phase j
S_{wi} Irreducible water saturation

Table I Recovery of Oil by ASP Flooding for Three Different Systems using SDS and SDS Derivative.

Sand Pack Sample No.	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		
		k_w (S_w=1)	k_o (S_{wi})				S_{wi}	S_{oi}	S_{or}
ASP2	36.805	1.144	0.212	0.3 PV (0.7% NaOH + 0.1% SDS + 2000 PPM PHPAM) + 0.2 PV 2000 PPM Buffer + Chase Water	50.2	24.446	17.500	82.500	20.125
ASP7	38.89 %	2.116	0.218	0.3PV(0.0078% SDS D + 0.7% NaOH + 2000 PPM PHPAM) + 0.2 PV2000 ppm PHPAM + Chase water	50.01	29.5	21.32	75.88	18.08
ASP8	37.72 %	2.012	0.221	0.3PV (0.0156% SDS D + 0.7% NaOH + 2000 PPM PHPAM) + 0.2 PV 2000 PPM PHPAM + Chase water	50.1	29.8	26.03	73.97	18.1

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