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Application of environmentally friendly nonionic surfactants in enhanced oil recovery at different field parameters

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Abstract

The depletion of crude oil in the world is a great problem facing the technological and industrial sectors all over the world. The gap between the required and present amounts of energy source can be compensated by several routes including: renewable energy, biofuel and recover of the crude oil from depleted oilfields. Several methods were used to recover the crude oils including the use of recovering solutions which form emulsions by the crude oil and can be easily extracted. In this study, environmentally friendly nonionic surfactants were applied as additives for formulation of recovery fluids in enhanced oil recovery process. The influence of the process parameters were studied including: surfactant concentration, pH of the medium, salinity and the chemical structure of the used surfactants. The obtained recovery efficiencies of the different surfactants were ranged between 27-65% in the presence of the most effective derivative of Sorbitan Esters. The efficiency of the recovery process was extremely influenced by the studied parameters.

Keywords: nonionic surfactants; surface activity; enhanced oil recovery; emulsion. Received; 23 Nov. 2020, Revised form; 26 Dec. 2020, Accepted; 26 Dec. 2020, Available online 1 Jan. 2021

1. Introduction

Unconventional energy sources have not yet presented appropriately to meet the energy request of the world; consequently, crude oil will play furthermore an important role in the energy consumption in the upcoming time. In view of the fact that the simply recoverable oil is running out and considerable amounts of oil remain in their reservoirs after conventional extraction methods. The application of Enhanced Oil Recovery (EOR) has become essential to guarantee a continuous crude oil supply. Some studies shown that sugar-based surfactants are effective surfactant because it can lower the IFT and have excellent adsorption at solid-liquid interface [1-2]. EOR technology includes the injection of specific type of fluids into the reservoir by several methods including chemical, thermal or microbial methods. The fluids stream removes the adhered crude oil in the bottom-rocks and sediments of the oilfield toward the producing well. Another research on EOR has shown that the IFT decreases as the saponin concentrations increase [3]. Generally, these fluids interact physically and/or chemically with the sediment layers and bottom-rocks reservoir saturated with crude oil and modifies the conditions of oil recovery. These interactions include depression of the oil-aqueous medium interfacial tension (IFT), increases the stream properties of the oil in the oil-water emulsions, increase the wettability of the socks surfaces which eases the crude oil separation from the rock pores and developing preferential phase behavior.

[4-5]. EOR is an important and interesting field, so large number of patents highlighted the significance of this field of study. Based on the studies in the last 20 years, the surfactants type additives were more efficient technologically and economically for a higher efficiency of the EOR than the reported technologies [6, 7]. Chemical flooding of depleted oil reservoirs is one of the most effective methods to increase the recovery rate of the oil from these reservoirs. Due to the expensive field tests of EOR, several screening test methods were expanded to decrease the economic cost and to estimate the effectiveness of the flooding solutions containing surfactants [3, 7, 8]. In this study, environmentally friendly nonionic surfactants were tested in formulation of flooding formulations of EOR process. The study involved the determination of the different conditions affect the EOR process including salinity, pH and surfactants concentration. The optimum conditions of maximum EOR efficiency were determined.

2. Materials and Experiments

2.1 Materials

Chemicals used in this study were: Sorbitol, phosphoric acid, ethylene oxide, triethyl amine, lauric, palmitic, stearic and oleic acid and were obtained from Sigma-Aldrich chemicals company, Egypt. The physical properties of the used crude oil were listed in *Table 1*.

Table (1): Physical properties	of the crude of used in the study		
Oil properties	Test	Value	
Average molecular weight (g/mol)	ASTM D-3606	187.9	
Density at 60 °F (g/cc)	ASTM D-4052	0.8419	
API gravity @ 60°F	ASTM D-4052	36.40	
Pour point, °C	ASTM D-97	36.34	
Wax content, wt.%	UOP-64	12.9	
Water content, ppm	ASTM D-95	60.8	
Sulfur content, wt%	ASTM D-4294	0.19	
Flash point, °C	ASTM D-93	3	
Total Acid Number, mg KOH/gm.	ASTM D-664	0.4435	
2.2. Synthesis of Sorbitan Esters	(1 mol) was introduced into the flask an	d after melting	

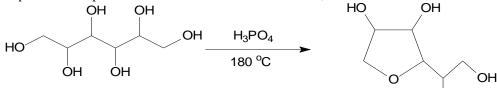
Table (1). Physical properties of the crude oil used in the study

2.2. Synthesis of Sorbitan Esters

The synthesis of Sorbitan Esters was preceded through three reaction steps, which were described below.

2.2.1. Dehydration of Sorbitol to Sorbitan

Sorbitol was dehydrated using phosphoric acid in the following typical procedure to produce sorbitan. Sorbitol



for one hour; scheme 1.

Scheme 1: Dehydration of Sorbitol to Sorbitan.

2.2.2. Preparation of Sorbitan Esters

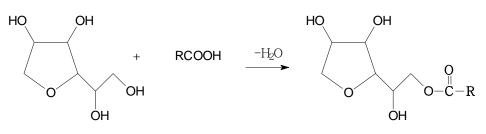
Sorbitan esters were reacted by different fatty acids individually to obtain nonionic surfactants. Sorbitan (1 mol) and fatty acids namely: lauric (L), palmitic (P), stearic (S) and oleic (O) acid (1.2 mol) were added individually and sodium hydroxide (15 mmol) in the reaction vessel. The temperature of the reaction was adjusted at 140 °C under stirring, until the water of the reaction was started to obtain. After 4 h, the water was completely distilled off (21.1 mL), and the reaction mixture was stirred for 1 h at 150 °C, and the reaction product was allowed to cool to room temperature. The obtained ethoxylated sorbitan laurate E(20)SL, ethoxylated sorbitan palmitate E(20)SP, ethoxylated sorbitan stearate E(20)SS and ethoxylated sorbitan oleate E(20)SO were obtained from the esterification products of sorbitan and lauric, palmitic, stearic and oleic acid, respectively; scheme 2.

OH

(100-110 °C) and the stirring was switched on; then

phosphoric acid (2.5 mmol) was added and the temperature was raised to 180 °C. Water was distilled off

during 3 h, and the reaction mixture was stirred at 180 °C

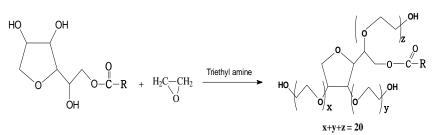


R= C₁₁H₂₃, C₁₅H₃₁, C₁₇H₃₅, C₁₇H₃₃ Scheme 2: Esterification of Sorbitan.

2.2.3. Ethoxylation of Sorbitan Esters

The reaction between sorbitan esters and ethylene oxide was carried out following the procedures of Ref. [9]. In a typical experiment, 1 mole of sorbitan esters (individually) was charged into the reaction system in presence of 1% triethyl amine as a catalyst and then was heated to 150-180 °C with continuous stirring. A stream of nitrogen gas firstly was passes through the system for 2 minutes to flush out air. The nitrogen stream was then replaced by ethylene oxide stream at a fixed rate, which was regulated by monitoring the Hg-level of the manometer. The reaction was carried out for different time intervals after

which the apparatus was filled with nitrogen, cooled and weighed. After cooling, the obtained product was discharged, weighed and the catalyst was evaporated under vacuum (0.1 mm Hg, at 100 °C). The obtained ethoxylated products were white to pale yellow viscous liquids. The differences in weights indicate the amount of the ethylene oxide units consumed in the reaction, hence, the number of moles of ethylene oxide (n) attached to each mole of the reactants was calculated. The average number of ethylene oxide units attached was ranged between 19 and 20 units scheme 3.



R= C₁₁H₂₃, C₁₅H₃₁, C₁₇H₃₅, C₁₇H₃₃

Scheme 3: Preparation of Sorbitan Esters Nonionic Surfactants.

2.3. Evaluation of the prepared Sorbitan Esters in EOR process

2.3.1. Sandstone preparation procedure

The cleaning procedure of the used sandstone involves acid washing with hot hydrochloric acid to remove soluble metals, including iron, manganese, aluminum and others, and then washed thoroughly by water to reach the neutral. The pore throats size of in sandstone was ranged between 0.5 and 5.0 μ m, with average size of 1-0.5 mm [10]. The physical properties of the sandstone used in the study were determined [11-15] and listed in Table 2.

Table (2): Characterization of the used sandstone	
Sand properties	Value
Average sand particle size, mm	1-0.5
Sand density, g/cc	2.7
Average pore radius (µm)	3.9
Porosity (%)	35.8
2.3.2. Measurement of surface tension, interfacial surfactant solutions to obtain c	ertain reservoir parameters

2.3.2. Measurement of surface tension, interfacial tension and contact angle

Surface tension values of the used nonionic surfactants in their solutions were measured using Kruss-K6 tensiometer, GmbH, Germany, using Du-Nouy deattached platinum ring method at 25 °C. The platinum ring was washed using acetone and dried by flame after each measurement. A mean of three readings was considered at each surfactant concentration. The values of the surface tension were plotted against the concentration to obtain the surface tension-concentration profile of each nonionic surfactant. Critical micelle concentration (CMC) of each surfactant was determined by extrapolation method. Interfacial tension measurements were performed between crude oil and surfactant solutions (0.1% wt) at 25 °C.

Contact angle was measured using Attension Theta High Pressure optical tensiometer. The contact angles of the different solutions were measured at concentration of 0.1 wt% at 25 $^{\circ}$ C.

2.3.3. Foaming properties nonionic surfactants

Foaming power experiments of the tested surfactants were conducted in a graduated measuring cylinder with 0.5 wt% solution at 25 °C. The tests were performed using bottle shaking tests (ASTM D-3601). For foam study, a constant volume of the aqueous sample in a 10 mL graduated centrifuge tube was shaken manually at a fixed frequency for fixed time (15 min) and then left untouched on a flat surface [16-19]. The foaming power of the surfactant solution was measured by considering the initial foam volume after constant time at 25 °C.

2.3.4. Preparation of sandstone/crude oil saturated system

The saturated sandstone by crude oil system was prepared by mixing 250 g of sandstone and 150 mL of crude oil for 24 h at 40 °C. The sand holder was prepared by installing all fittings and pressure testing for leaks. The sandstone flooding experiments carried out as described in the literature [20] with brine solution, crude oil and surfactant solutions to obtain certain reservoir parameters such as porosity, permeability, initial oil and water saturation.

2.3.5. Experimental procedures of crude oil flooding

The procedures of crude oil flooding using the tested nonionic surfactants were performed as follows:

- a. 250 mL of surfactant solutions with different concentration (0.01 0.3 g/L) were used.
- b. the surfactants solutions were prepared in different salinity aqueous medium (0-100000 ppm).

c. the medium of the treatment was changed between alkaline to acidic (pH=5-9).

In the first of the experiment, a preliminary test was performed using the four nonionic surfactants at concentration of 0.1 g/L at pH 7 to determine the best crude oil recovery using these surfactants.

The stock tank oil was injected at a rate of 60 ml/h by displacement pump until the water production ceased. Crude oil permeability at initial water saturation (Swi) was also measured. During the oil injection process, the sand pack was heated to 70°C to simulate actual reservoir condition. The sandstone was allowed for 2 days to attain equilibrium under reservoir conditions and overburden pressure of 500 psi was applied to the sandstone during aging time and flooding conductance. The purpose of this aging procedure was to change the wettability of the sandstone to oil-wet. After oil injection, the sand pack was brine flooded. Brine injected was until the oil production became negligible. At this stage recovered oil by primary and secondary method is exhausted. After brine injection, about 3 pore volume (PV) for chemical solution was injected and left about 24 hours, followed by an extended water flood until oil cut at the outlet became less than 1 %. The oil production was determined on a volume basis to calculate recovery percentage. The recovery factor was calculated by two methods, either using a secondary oil displacement procedure or by means of tertiary oil. The amount recovered was calculated via a mass balance equation as follows:

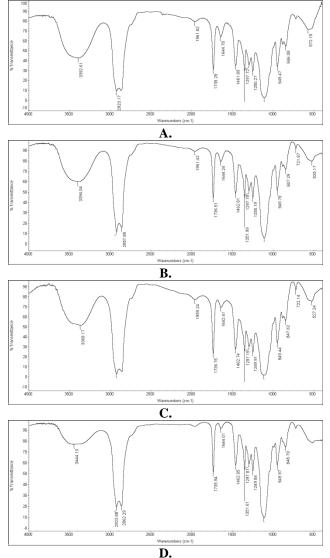
Volume of oil remaining in the sand pack = injected oil volume – expelled oil volume

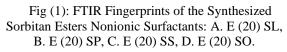
The recovery factor is obtained by summing up the amount of oil recovered in each step (secondary and tertiary process).

3. Results and Discussion

3.1. Chemical structures of the prepared Sorbitan Esters

The chemical structures of the prepared Sorbitan Esters were determined using FTIR spectroscopic analysis, **Figure 1**. The obtained compounds were showed the following absorption bands: 3200-3600 cm⁻¹ centered at 3400 cm⁻¹ corresponded to O-H stretching vibration, 2850 and 2920 cm⁻¹ corresponded to symmetric and asymmetric stretching vibration of C-H bonds, 1735 cm⁻¹ related to carbonyl ester groups and 1100 cm⁻¹ assigned for C-O-C ether linkages. Comparing the fingerprints of the prepared Sorbitan Esters by the published data proved their expected chemical structures as represented in Scheme 3.





3.2. Surface and interfacial properties of nonionic Sorbitan Esters surfactants

The surface and interfacial properties of the surfactants used in the oil field are very important due to their interaction by the oil and the operation systems in the crude oil processing determine their applicability in the different operations. Figure 2 represents the surface tension-concentration profile of the nonionic surfactants under consideration at 25 °C [21-24].

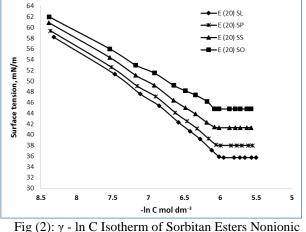


Fig (2): γ - ln C Isotherm of Sorbitan Esters Nonionic Surfactants.

It is clear that the gradual increase in the molecular weight of the different Sorbitan Esters surfactants increases the surface tension of their solutions [25]. Also, increasing the concentration of the surfactants in their aqueous medium gradually decreases their surface tension to reach to the stabilization at characteristic concentration. The surface tension depression stabilized at the corresponding critical micelle concentration of each surfactant, which were determined and listed in Table 3. The adsorption of the surfactant molecules on the surfaces can be determined from their surface pressure and the maximum surface excess values [26], Table 3. The critical micelle concentration values of the studied nonionic surfactants showed gradual decrease in their values by increasing their molecular weight to reach to the minimum for E (20) SO at 0.125 mM [27]. The maximum surface excess values also were decreased gradually from E (20) SL to E (20) SO. Furthermore, the calculated minimum surface area occupied by surfactant molecules at the interface showed that the maximum area was occupied by E (20) SO at 47 $Å^2$. The interfacial tension of the surfactant solution determines it ability to emulsify the organic phase in the aqueous phase and also determines the stability of the formed emulsions [28-30]. Lower IFT values indicates the high tendency of the surfactant solution to emulsify the organic (oil) phase and also high stability of the formed emulsion, while moderate IFT values revealed the high emulsifying power of the surfactant solution accompanied by low emulsion stability formed. The Hydrophile Lipophile Balance (HLB) of surfactants determines the ability of surfactant molecules to dissolve in the oil phase. The lower the HLB value the more lipophilic or oil soluble the surfactant is, while the higher the HLB value the more water soluble or hydrophilic the surfactant is. The values of HLB of the

studied surfactants were listed in Table 3. It is clear that all of the studied surfactants are oil soluble with different ratio. E (20) SL has HLB of 16.7 and E (20) SO has HLB

of 14.3. That indicates the higher solubility of E (20) SO in the oil phase than E (20) SL , E (20) SP , E (20) SS .

Table 3: Surface and Interfacial Properties of the Studied Nonionic Surfactants at 25 °C						
Surfactant	$ln(CMC.10^3)$	Γ_{\max}	$A_{min,}$	IFT	HLB	Foaming power, mL
Surractant	mol.dm ⁻³	mmol/m ²	nm ² /molecule	mN/m	TILD	(ASTM D-3601)
E (20) SL	2.606	6.341	26.1	12.35	16.7	60
E (20) SP E	2.493	5.451	32.4	11.43	15.6	74
(20) SS E	2.440	4.236	39.6	10.23	15.0	80
(20) SO	2.290	3.469	47.8	8.74	14.3	37

able 3: Surface and Interfacial Properties of the Studied Nonionic Surfactants at 25 °C

The application of surfactants solutions in the crude oil applications has high restrictions due to the ability of highly stable emulsion formation which cannot be easily demulsified and consequently increases the economics of the process. The surface activity study of the used nonionic surfactants revealed that E (20) SL, E (20) SP, E (20) SS has higher CMC values than E (20) SO which indicates their higher tendency to foaming during the process [31]. The formation of foam during the process is discouraged due to it increases the pressure of the pipes which caused serious side effect and may be pipeline shutdown. The maximum surface activity of E (20) SO showed its moderate adsorption at the solid/aqueous solution interface. The adsorption at the interfaces leads to wetting of the interface (aqueous/solid interface) and consequently increases the detachment of organic compounds (mainly adsorbed crude oil) from the rocks surface [32]. The interfacial tension values of the studied nonionic surfactants were comparatively low, which showed their high tendency to emulsify crude oil with different stability degree of the formed emulsion. IFT value of E (20) SO was found at 8.74 mN/m, which is slightly lower than the other nonionic surfactants under consideration. That showed the higher stability of the oil emulsions formed in the presence of E (20) SO surfactant. The HLB values of the studied nonionic surfactants were varied between 16.7 and 14.3, which showed their gradual change in their properties towards the interaction by the crude oil [33-38]. E (20) SO has HLB value of 14.3, which indicates its higher tendency to dissolve in the oil phase than E (20) SL , 40, 60. The lowest foaming power was pointed also for E (20) SO at 37%, which was lower than the other studied surfactants.

The review of the surface and interfacial properties of the different nonionic surfactants under investigation (E (20) SL, E (20) SP, E (20) SS, E (20) SO) indicates their high performance in emulsification and solubilization processes of crude oil, with high preferential for, E (20) SO. That can be rationalized to its lower CMC value, interfacial tension and foaming formation, in addition to its high emulsification tendency and the lower stability of the formed emulsion during its application. Also, the lower tendency to foam formation compared to E (20) SL, E (20) SP, E (20) SS under investigation. That encourages our study to direct towards application of E (20) SO solution in flooding of crude oil from sandstone during enhanced oil recovery (EOR) process [39-42].

3.3 Recovery of crude oil using Sorbitan Esters nonionic surfactants

Screening of the studied Sorbitan Esters during the EOR of crude oil from saturated sandstone using 0.002-0.35 g/L surfactants solutions at pH 7 in pure water indicated that their recovery efficiencies were increased by increasing the molecular weights of the surfactants used. The efficiency was calculated based on the separated volume of the crude oil separated from the obtained crude oil/aqueous emulsion after 2 h settling at 25 °C. This can be considered as a reasonable judgment on the efficiency of studied surfactants, because this measurement considers the flooding of the crude oil from the sandstone and also the stability of the formed emulsion. Stable crude oil/aqueous solution emulsion is not favored during the process, while fast demulsified emulsion is the best. E (20) SO showed the highest recovery of 65.2%. The considerable high EOR process efficiency is due to the high porosity of the sand pack (37%), and consequently water flooding is able to produce high recovery (65.2%) [43-48].

Based on the screening test of the studied nonionic surfactants, E (20) SO was extensively studied in the EOR process of crude oil from sandstone and determining the influence of the wide range surfactant concentration, salinity of the flooding system and pH of the medium.

3.3 Effective parameters on the EOR process

In this section, the influence of the different parameters on the EOR process of crude oil from sandstone including the surfactant concentration in the range of 0.02-0.35 g/L, pH of the medium in the range of 5-9, and salinity at 0-80000 ppm were studied.

3.3.1 Effect of surfactant concentration

Table 4 represents the EOR efficiency in the presence of different concentrations of E (20) SO nonionic surfactant in the flooding solution in neutral medium (pH=7). It is clear that the EOR efficiency is increased by increasing the surfactant concentration to reach to the maximum value at 65.2%.

Surfactant concentration,	Surfactant concentration,	EOR efficiency,
g/L	mol.dm ³	%
0.002	11.08	27.2
0.01	9.48	30.2
0.05	7.53	47.5
0.1	7.17	53.4
0.2	6.48	60.3
0.3	6.07	65.2
0.35	5.92	65.1

Table (4): Effect of E (20) SO concentration on the EOR process of crude oil

Figure 2 represents the variation of the surface tension of E (20) SO at the different concentrations used during the EOR process. It is clear that there is a gradual decrease in the surface tension values by increasing the concentration from 0.002 g/L to 0.35 g/L. The decrease in the surface tension revealed the increase in the interaction between the surfactant solution and the sandstone surface. Increasing the concentration of E (20) SO is considerably decreases the surface tension of the flooding solution and increases the interaction between the surfactant solution and the sand particle surface. That leads to wetting the sand surface, which releases the adsorbed crude oil to the effluent [49-50]. The low HLB value and lower interfacial tension of E (20) SO increases the ability of crude oil separation from the formed emulsion. The optimum amount of recovered crude oil was obtained in the presence of 0.3 g/L of E (20) SO solution at 65.3%, Table 4

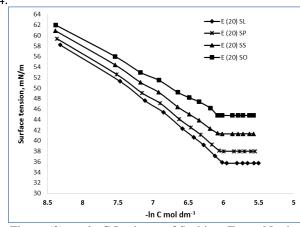


Figure (2): γ - ln C Isotherm of Sorbitan Esters Nonionic Surfactants.

3.3.2 Effect of salinity

The salinity of the nonionic surfactant solution has a great influence on its surface activity. Figure 3 represents the influence of the salinity on the surface tension-concentration profile of E (20) SO nonionic surfactant at 25 °C. It is clear that increasing the salinity of the medium increases the surface tension values considerably to reach to its maximum value at 80000 ppm. Increasing the surface tension values of E (20) SO solution at constant surfactant concentration by increasing the salinity indicates the decrease in the surface activity. The increase of salinity of the medium leads to salt-out of the nonionic surfactants from their solution. That leads to decrease the amount of dissolved E (20) SO molecules in the medium,

which raises the surface tension and lowers the surface activity.

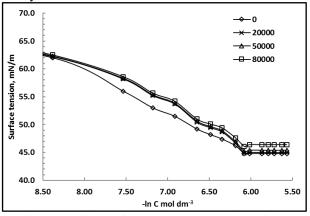


Fig (3): Variation of γ vs. –ln Concentration of E (20) SO at Different Salinity at 25 °C.

The effect of salinity on the EOR process efficiency is represented in Figure 4. It is clear from Figure 4 that the maximum EOR efficiency was obtained at 65.2% using 0.3 g/L surfactant concentration. Furthermore, the efficiency was obtained at 27% using 0.002 g/L at 0.0 ppm salinity. The gradual increase in the salinity of the medium from 20000 to 80000 ppm showed negligible to minor influence on the EOR process efficiency at the constant surfactant concentrations. This behavior can be explained based on the variation of the surface activity of E (20) SO solution at constant concentration under different salinities.

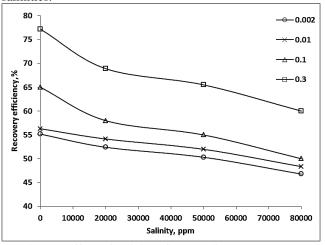


Fig (4): Effect of salinity of the medium on the EOR process efficiency at different E (20) SO concentrations.

The requirement of surface-active stability of the used surfactants during the flooding process is very important to regulate the recovery process under different salinity conditions. The salinity of the down hole is varied between 20000 to 150000 ppm depending on the types of sediments and the formation conditions. Mainly, the salinity of down hole during EOR processes is varied between 20000 to 100000 ppm. The stability of the surface activity of E (20) SO at different salinity was studied. It is clear from Figure 5 that the variation of the surface tension values of E (20) SO at constant concentration (0.002-0.3 g/L) by changing the salinity of the medium was almost stable and showed a negligible change. At constant concentration, the stability of surface tension values of E (20) SO solution by changing the salinity of the medium indicates the retaining of its high surface activity at the interface along the entire range of solution salinity.

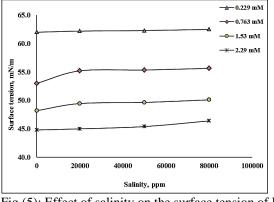
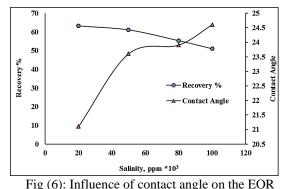


Fig (5): Effect of salinity on the surface tension of E (20) SO at the application range of concentration.

The recovery of the crude oil from the downhole sandstone depends on the efficiency of the flooding solution in wetting the stone. The wettability of the flooding system (in this case is E(20) SO) can be expressed in terms of contact angle and interfacial tension. Generally, flooding solutions with lower contact angles and interfacial tension values exhibit higher wettability for the surfaces. The wettability of the sandstone surface leads to penetrate the water between the particles and push the oil from the bulk and prevent the adhesion of the oil on this surface.

Figure 6 represents the influence of the contact angle of E (20) SO solution at different salinity of the flooding medium on the efficiency of EOR process. The relation between the contact angle and the recovery % is inverse relationship, while it is proportional between the contact angle and the salinity. Increasing the salinity of the medium increases the contact angle of the solution. That accompanied by decreasing the recovery of the crude oil from the stone. Increasing the contact angle indicates the decrease of the surface activity of the solutions as the salinity increased. Obviously, the lowest contact angle of the flooding solution, which corresponds to the highest surface activity, is joined by the highest recovery efficiency at 65.2%.



efficiency using E (20) SO at 0.3 g/L at different salinity.

Figure 7 represents the effect of the interfacial tension variation of the flooding solution (E (20) SO) on the recovery efficiency at different salinity. The interfacial tension of the flooding solution has a great influence on the flooding efficiency during the EOR process. Increasing the salinity of the medium increases the interfacial tension of the flooding solution to reach its maximum value of 10.8 mN/m at 100000 ppm salinity. The profile of recovery % in Figure 7 showed that the maximum recovery was obtained at the lowest interfacial tension values which presented at the lowest salinity.

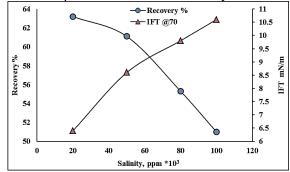


Fig (7): Influence of interfacial tension on the EOR efficiency using E (20) SO at 0.3 g/L at different salinity. **3.3.3 Effect of pH**

Figure 8 represents the variation of the EOR efficiency at different pH values of the flooding solutions. It is clear that the maximum process efficiency was obtained at neutral medium of pH 7. It is also obvious from Figure 8 that the acidic and alkaline medium has slightly negative impact on the EOR process efficiency. Comparing the process efficiencies in acidic and alkaline media revealed that the recovering efficiency in the alkaline medium is slightly higher than that of the acidic medium [51-52].

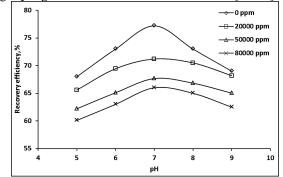


Fig (8): Effect of pH of the medium on the EOR process efficiency using E (20) SO solution.

That can be described from the relation between the surface activity and the pH of the medium of the flooding process. Figure 9 represents the relation between the surface tension of E (20) SO surfactant solution at different concentration and the pH of the medium.

It is clear from Figure 9 that the surface tension values of E (20) SO in alkaline medium are comparatively lower than those in the acidic media. That can be attributed to the interaction between the polyethylene glycol chains and the hydroxide ions and also by the hydronium ions. Hydronium ions (H_3O^+) are attracted to the lone pairs of the oxygen atoms in the polyethylene glycol chains, which decreases the hydrogen bonds between the nonionic surfactant and the water molecules. That decreases their solubility in the aqueous medium, which decreases the surface activity of their solutions. Consequently, their interfacial and wetting activities are decreased. The decreases the recovery efficiency as the flooding effect of the solution is decreased [53].

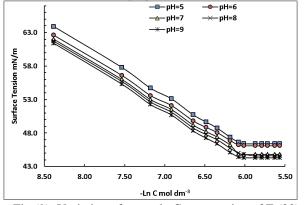


Fig (9): Variation of γ vs. –In Concentration of E (20) SO at Different pH Values at 25 °C.

In alkaline medium, the interaction between the E (20) SO molecules and the hydroxide ions (OH⁻) is repulsive, which increases the interaction between the surfactant and water molecules. That increases the surface activity of the

References

[1] S. Thomas "Enhanced Oil Recovery-An Overview. Oil & Gas Science and Technology", (2008) 63, 9-19.

[2] N. Gaillard, B. Giovannetti, and C. Favero "Improved Oil Recovery Using Thermally and Chemically Protected Compositions Based on Co- and Terpolymers Containing Acrylamide". SPE Improved Oil Recovery Symposium, (2010) Tulsa, 24-28 April 2010, Document ID: SPE-129756-MS.

[3] D. B. Levitt, and G.A. Pope "Selection and Screening of Polymers for Enhanced-Oil Recovery". SPE Symposium on Improved Oil Recovery, (2008) Tulsa, 20-23 April 2008, Document ID: SPE-113845-MS.

[4] C. Zhong, P. Luo, Z. Ye, and H. Chen "Characterization and Solution Properties of a Novel Water-Soluble Terpolymer for Enhanced Oil Recovery". Polymer Bulletin 62 (2009) 79-89. surfactant solution. That can be observed from the lower surface tension values of E (20) SO solution at various concentrations in alkaline medium, Figure 9. Increasing the surface activity of E (20) SO solution in alkaline medium increases its interfacial and wetting power [54, 55], which increases its flooding efficiency. In neutral medium, the EOR process efficiencies were at the maximum value, which can be attributed to the balance between the interaction and repulsion occurred between the surfactant and water molecules. That effect was studied at a wide range of salinity and the results revealed the same behavior at the salinity range.

Figure 10 showed the variation of the surface tension of E (20) SO at different pH values using the concentration of the EOR process of the study. It is clear that the variation of pH of the medium has no significant effect on the surface activity of the flooding solution of E (20) SO. The stability of the surface tension values explains the narrow differences between the recovering efficiencies of E (20) SO at the used concentration range during the entire pH range.

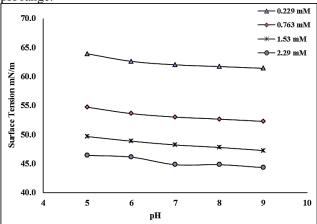


Fig (10): Effect of pH of the medium on the surface tension values of E (20) SO during the application range.

[5] L.L. Schramm "Surfactants: Fundamentals and Applications in the Petroleum Industry" Cambridge University Press, Cambridge, (2000) 8-15.

[6] D. Myers, "Surfactant Science and Technology", third ed., (2006), 380 pp.

[7] Z. Jeirani, B. Mohamed Jan, B. Si Ali, I.M. Noor, C. H. See, and W. Saphanuchart "Formulation, Optimization and Application of Triglyceride Microemulsion in Enhanced Oil Recovery". Industrial Crops and Products, (2013) 43, 6-14.

[8] H. A. Nasr-EI-Din, B. F. Hawkins, and K. A. Green, "Recovery of Residual Oil Using the Alkali/Surfactant/ Polymer Process: Effect of Alkali Concentration". Journal of Petroleum Science and Engineering, (1992) 6, 381-401.

[9] AN. Wrigley, FD. Smith, AJ. Stirton "Synthetic detergents from animal fats VIII. The ethoxylation of fatty acids and alcohols". J. Am. Oil Chem. Soc. (1957) 34, 39–43.

[10] V. T. Stephanie, and P. Marc "evaporation of sodium chloride solution from a saturated porous media with efflorescence formation" journal of fluid mechanics, (2014) 749, 701.

[11] KA. Elraies, IM. Tan, M. Awang "A new approach to low-cost, high performance chemical flooding system". In: SPE production and operation conference and exhibition, (2010) June 8–10, Tunis, Tunisia.

[12] AK. Flaaten, QP. Nguyen, J. Zhang "Alkaline/surfactant/polymer chemical flooding without the need for soft water". SPE J. 15, (2010) (1):184–96.

[13] R. Kumar, KK. Mohanty "ASP flooding of viscous oils". In SPE annual technical conference and exhibition, (2010) September 19–22, Florence, Italy.

[14] VC. Santanna, FDS. Curbelo, TN. Castro Dantas "Microemulsion flooding for enhanced oil recovery". J Pet Sci Eng.; 66(3–4): (2009) 117–20.

[15] JG. Southwick, Y. Svec, G. Chilek "The effect of live crude on alkaline–surfactant–polymer formulations: implications for final formulation design". In: SPE annual technical conference and exhibition, (2010) September 19-22, Florence, Italy.

[16] A. R. Kovscek and C. J. Radke "Fundamentals of Foam Transport in Porous Media" American Chemical Society; Chapter 3 (1994) p115-163.

[17] T. Tamura, Y. Kaneko "Foam film stability in aqueous systems. In: Hartland S, editors. Surface and interfacial tension: measurement, theory, and applications". Surfactant Science Series 119, CRC Press, New York, (2004) p. 90.

[18] RAK. Nadkarni "Guide to ASTM test methods for the analysis of petroleum products and lubricants". ASTM manual series; no. mnl44-2nd, West Conshohocken, PA, (2007) p. 111.

[19] M. Moayedi, LA. James, M. Mahmoodi "An experimental study on optimization of SAG process utilizing nonionic surfactants and sodium lignosulfonate". In: International symposium of the society of core analysts, 8–11 September Avignon, France, SCA(2014)-087.

[20] DL. Zhang, L. Shunhua, M. Puerto, "Wettability alteration and spontaneous imbibitions in oil-wet carbonate formations" J Pet Sci Eng.;52(1–4): (2006) 213–26.

[21] E. Hoff, B. Nystrom, B. Lindman "Polymer– surfactant interactions in dilute mixtures of a nonionic cellulose derivative and an anionic surfactant". Langmuir. ;17(1):(2001) 28–34.

[22] A. Bera, S. Kumar, A. Mandal, "Temperaturedependent phase behavior, particle size and conductivity of middle-phase microemulsions stabilized by ethoxylated nonionic surfactants" J Chem Eng Data. ; 57(12): (2012) 3617–3623.

[23] P. Jiang, N. Li, J. Ge "Efficiency of a sulfobetainetype surfactant on lowering IFT at crude oil-formation water interface" Colloids Surf A. (2013) 443:141–8.

[24] KM. Ko, BH. Chon, SB. Jang "Surfactant flooding characteristics of dodecyl alkyl sulfate for enhanced oil recovery". J Ind Eng Chem.;20(1): (2014) 228–33.

[25] DL. Zhang, L. Shunhua, M. Puerto "Wettability alteration and spontaneous imbibitions in oil-wet carbonate formations" J Pet Sci Eng.; 52(1–4): (2006) 213–26.

[26] Y. Wu, PJ. Shuler, M. Blanco "An experimental study of wetting behavior and surfactant EOR in carbonates with model components" In: SPE/DOE symposium on improved oil recovery, (2006) April 22–26, Tulsa, Oklahoma.

[27] T. Babadagli "Analysis of oil recovery by spontaneous imbibitions of surfactant solution". Oil Gas Sci Technol Rev.; 60(4): (2005) 697–710.

[28] T. Babadagli, Y. Boluk "Oil recovery performances of surfactant solutions by capillary imbibitions" J Colloids Interface Sci.; 282(1): (2005) 162–75.

[29] M. El-Batanoney, T. Abdel-Monghny, M. Ramazi "The effect of mixed surfactants on enhancing oil recovery" J Surfactants Deterg. 2(2): (1999) 201–5.

[30] Y. Gong, Z. Li, J. An "The properties of sodium naphthalene sulfonate in lowering interfacial tension and its possibility of application in EOR" J Dispersion Sci Technol.; 26(4): (2005) 503–7.

[31] A. Bera, K. Ojha, A. Mandal "Synergistic effect of mixed surfactant systems on foam behavior and surface tension" J Surfactants Deterg. 16(4): (2013) 621–30.

[32] D. Huang, A. Nimolvo, D. Wasan "Foams: basic properties with applications to porous media". Langmuir. 2(5): (1986) 672–7.

[33] Z. Aktas, JJ. Cilliers, AW. Banford "Dynamic froth stability: particle size, airflow rate and conditioning time effects". Int J Miner Process. 87(1–2): (2008) 65–71.

[34] Z. Du, MP. Bilbao-Montoy, BP. Binks "Outstanding stability of particle-stabilized bubbles". Langmuir 19(8): (2003) 3106–8.

[35] TS. Horozov "Foams and foam films stabilized by solid particles". Curr Opin Colloid Interface Sci. 13(3): (2008)134–40.

[36] S. Ata "Coalescence of bubbles covered by particles" Langmuir. 24(12): (2008) 6085–91.

[37] A. Dippenaar "The destabilization of froth by solids. II. The ratedetermining step" Int J Miner Process. 9(1): (1982) 15–22.

[38] GC. Frye, JC. Berg "Antifoam action by solid particles" J Colloid Interface Sci.;127(1): (1989) 222–38.

[39] BP. Binks, SH. Tommy "Aqueous foams stabilised solely by silica nanoparticles" Angew Chem Int Ed Engl.;44(24): (2005) 3722–5.

[40] A. Dippenaar "The destabilization of froth by solids. I. The mechanism of film rupture" Int J Miner Process. 9(1): (1982) 1–14.

[41] UT. Gonzenbach, AR. Studart, E. Tervoort "Ultrastable particlestabilized foams" Angew Chem Int Ed.; 45(21): (2006) 3526–30.

[42] S. Zhang, D. Sun, X. Dong "Aqueous foams stabilized with particles and nonionic surfactants" Colloids Surf A.; 324(1–3): (2008) 1–8.

[43] R. Aveyard, BP. Binks, PD. Fletcher "Aspects of aqueous foam stability in the presence of hydrocarbon

oils and solid particles" Adv Colloid Interface Sci.; 48: (1994) 93–120.

[44] R Aveyard, BP. Binks, PD. Fletcher "Contact angles in relation to the effects of solids on film and foam stability" J Dispers Sci Technol.; 15(3): (1994) 251–71.

[45] DR. Exerowa, PM. Kruglyakov "Foams and foam films" Amsterdam: Elsevier (1998) 98-120.

[46] JF. Sadoc, N. Rivier "Foams and emulsions" NATO ASI series 354 (1999) 90-99.

[47] NJ. Shirtcliffe, G. McHale, MI. Newton "Intrinsically super hydrophobic organosilica sol-gel foams" Langmuir.; 19(13): (2003) 5626–31.

[48] G. Zochhi, G. Broze, editors. "Handbook of detergents, part A properties". Surfactant science series. 59-(1999) Marcel Dekker, New York.

[49] A. Bera, A. Mandal, T. Kumar "Effect of rockcrude oil-fluid interactions on wettability alteration of oil-wet sandstone in presence of surfactants". Pet Sci Technol.; 33(5): (2015) 542–9.

[50] A. Bera, S. Kissmathulla, K. Ojha "Mechanistic study of wettability alteration of quartz surface induced

by nonionic surfactants and interaction between crude oil and quartz in presence of sodium chloride salt". Energy Fuels.; 26(6): (2012) 3634–43.

[51] K. Lunkenheimer, K. Malysa "A simple automated method of quantitative characterization of foam behaviour" Polymer Int.; 52(4): (2003) 536–54.

[52] E. Carey, C. Stubenrauch "Properties of aqueous foams stabilized by dodecyl trimethyl ammonium bromide" J Colloid Interface Sci.; 333(2): (2009) 619–27.

[53] JI. Kroschwitz Kirk-Othmer "encyclopedia of chemical technology" 4th ed. (1994) 155-175 New York: Wiley.

[54] G. Kaptay "Interfacial criteria for stabilization of liquid foams by solid particles" Colloids Surf A.; 230(1–3):(2004) 67–80.

[55] GN. Sethumadhavan, AD. Nikolov, DT. Wasan "Stability of liquid films containing monodisperse colloidal particles" J Colloid Interface Sci.; 240(1): (2001) 105–12.