Journal of Basic and Environmental Sciences

ISSN
Online:2356-6388
Print:2536-9202

Research Paper Open Access

Non-ionic Surfactants as Enhancement Oil Recovery based on Oleic Acid as Commercial Raw Material.

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Abstract:

Crude oil is limited and non-renewable. But despite this, the quantity of crude oil on hand must meet the increasing global requirements. Reduction of oil production has caused serious oil crises followed by a rise in oil prices. All these causes prompted the oil industry to extract oil from more challenging locations, where access is more difficult, and recovery methods are continually being improved. This has led to the advancement of enhanced oil recovery (EOR) techniques. The oleic acid as the model to prepared non-ionic surfactant by reacting with glycols derivatives to produce Alkoxy ethylated oleate used for enhanced oil recovery which showed higher efficiency.

Key words: enhanced oil recovery (EOR), Non-ionic, Surface properties.

1-INTRODUCTION:

Crude oil is finite and non-renewable. Despite this limitation, the available supply must meet the growing global demand. Reductions in oil production have led to significant oil crises, followed by rising prices. These challenges have driven the oil industry to extract oil from more complex and less accessible locations, necessitating continuous advancements in recovery techniques. This situation has spurred the development of enhanced oil recovery (EOR) methods. Currently, more than 66% of the oil discovered worldwide remains unrecovered after conventional production methods—namely, primary and secondary techniques. Primary recovery relies on natural energies within the reservoir, such as expansion, compaction, gas drive, solution gas drive, and natural water drive. The secondary recovery phase involves injecting water at strategic points in the reservoir to displace oil towards production wells. However, due to oil bypass and capillary forces, approximately 40-70% of the original crude oil remains trapped in place. Thus, EOR is necessary to improve production, as the remaining oil is confined within the pore structure of the reservoir. EOR encompasses various advanced recovery techniques, and our research focuses on one of these methods: non-ionic surfactant flooding. This technique is based on the phase behavior properties within the reservoir in relation to non-ionic surfactants and oil/brine systems. Our present work, focused on utilization of fatty matter extracted from oily wastes, for synthesis of the non-ionic surfactants which can be injected to the oil wells to achieve maximum oil recovery, and the economic feasibility of Non-ionic surfactants that synthesized from oily wastes. Non-ionic surfactants which are widely used in industries such as personal care [4], household products [5], and agrochemicals [6] are valued for their surface properties like emulsification, wetting, and dispersion [7]. They have become essential in applications like detergents, cosmetics, and pharmaceuticals due to their versatility and effectiveness in emulsification, dispersion, dissolution, and stabilization [8]. Non-ionic surfactants offer versatility and find applications across various functions, such as emulsification, dispersion, solubilization, and stabilization [9]. In recent years, there has been a significant increase in the popularity and widespread use of non-ionic surfactants [4] due to their effectiveness, low toxicity, and biodegradability [10]. Non-ionic surfactants are preferred over anionic and cationic surfactants because they are mild, low foaming, and compatible with other ingredients [11]. These surfactants are often produced using fatty acids derived from oily wastes refining processes [12]. Wastes oil refineries generate significant amounts of fatty acids as by-products [13], These raw materials can be effectively utilized for the production of non-ionic surfactants. [14]. The utilization of fatty acids obtained from wastes generated during the refining of oily wastes to produce non-ionic surfactants presents a sustainable and eco-friendly solution. This method reduces dependency on non-renewable resources and offers a valuable use for wastes materials, thereby enhancing their value and utilization [15]. Non-ionic surfactants based on fatty acids [16] provide a sustainable and efficient alternative to petroleum-derived surfactants [17]. By adjusting the composition of fatty acids, it is possible to customize the properties of these surfactants [18], degree of unsaturation, and molecular weight [19]. By utilizing fatty acids from renewable sources like oily wastes refinery wastes [20], the development of non-ionic surfactants with improved performance and reduced environmental impact is possible [21]. Using fatty acid refinery wastes from oily wastes [22] not only reduces wastes but also conserves resources and minimizes greenhouse gas emissions associated with the production of petroleum-based surfactants [23] oil wastes refineries generate substantial amounts of fatty acids as by-products [24]. These fatty acids can be efficiently utilized as raw materials for preparing nonionic surfactant which will be used for EOR (Enhanced Oil Recovery).

2-Material and instrumental:

2.1. Materials

Oleic acid was obtained from Sigma Aldrich. Diethylene glycol purchased from ADVENT, Tetra ethylene glycol and Hexa ethylene glycol purchased from Alfa Aesar. (p-Toluene sulfonic acid and Sodium Sulfate anhydride) were purchased from Sigma-Aldrich Chemicals Co. High-grade solvents including methanol and petroleum ether (40-60°C) obtained from Fisher.UK. Benzene and Sodium was purchased from El-Nasar Co. (Butyl Bromide, Iso-butyl Bromide, Tert-butyl Bromide) were purchased from Alfa Aesar.

2.2. Synthesis of esterified fatty acid nonionic surfactants

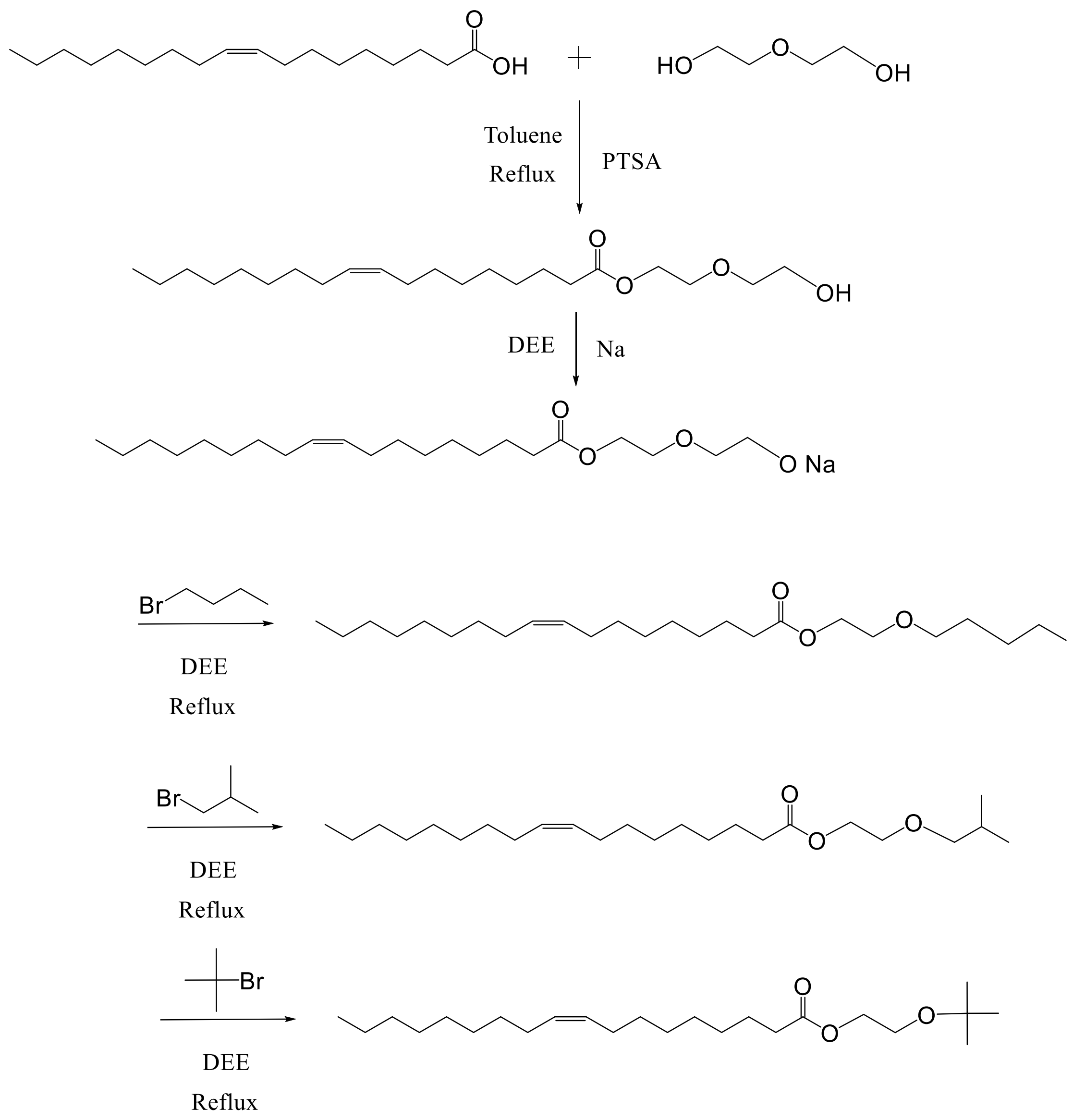
The synthesis of esterified fatty acid nonionic surfactants from oleic was carried out through the following series of steps (Scheme 1).

2.2.1. Synthesis of fatty acids monoester.

A mixture containing 0.1 mol of oleic acid and 0.1 mol of polyethylene glycol was refluxed in dry toluene, using 0.01% p-toluene sulfonic acid as a catalyst. The reaction involved performed under Dean-Stark trap conditions until the anticipated amount of water was separated. Subsequently, the resulting mixture was neutralized using sodium carbonate and subsequently washed twice with distilled water. Afterward, the mixture dried with anhydrous sodium sulphate, and the solvent was evaporated via distillation [25]. The structures of the synthesized monoesters were confirmed using Fourier-transform infrared spectroscopy (FTIR) [26].

2.2.2. Synthesis of Alkoxide ester:

Alkoxide ester was prepared by reacting of (0.005mole ;1.91gm.) of ester with (0.005mole; 0.115 gm) of sodium in 10 mL. diethyl ether as solvent. The mixture was stirred for 24 hours at room temperature.



Scheme 1

2.2.3. Synthesis of nonionic surfactant:

Nonionic surfactant was prepared by reaction of 0.6 gram of ester salt with 0.21 gram of butyl bromides (normal-butyl bromide, iso-butyl bromide and tert-butyl butyl bromide) was dissolved in 20 mL diethyl ether at 80°C.

2.2. Instrumentation:

1- The FTIR spectra of the compounds were recorded as liquids or solids in KBr disks using a Thermo Nicolet iS10 FTIR spectrophotometer at the Faculty of Science, Benha University, Benha, Egypt.

2- 1H NMR Spectra were obtained using a Bruker Avance (III) 400 MHz spectrometer (Switzerland) with 128 scans at 298 K, in deuterated DMSO (DMSO-d6) and/or CDCl3 as the solvent, with tetra methyl silane (TMS) used as an internal reference.

3- De-Noüy ring Tensiometer (Kruss-K6) was used to measure the surface tension of water at various molar concentrations of the prepared surfactant solutions

3.RESULTS AND DISCUSSION:

3.1. Characterization

3.1.1. The FTIR spectra of the ester (TEG).

The FT-IR spectra verify the presence of the anticipated functional groups in the synthesized ester, as depicted in Figure-1. These functional groups are indicated by the characteristic bands observed at 2919 and 2852 (ν_{C-H} aliphatic), 1733 ($\nu_{C=O}$), 1600 ($\nu_{C=C}$ stretch aliphatic fatty chain), and 1002 (ν_{C-O-C} stretching).

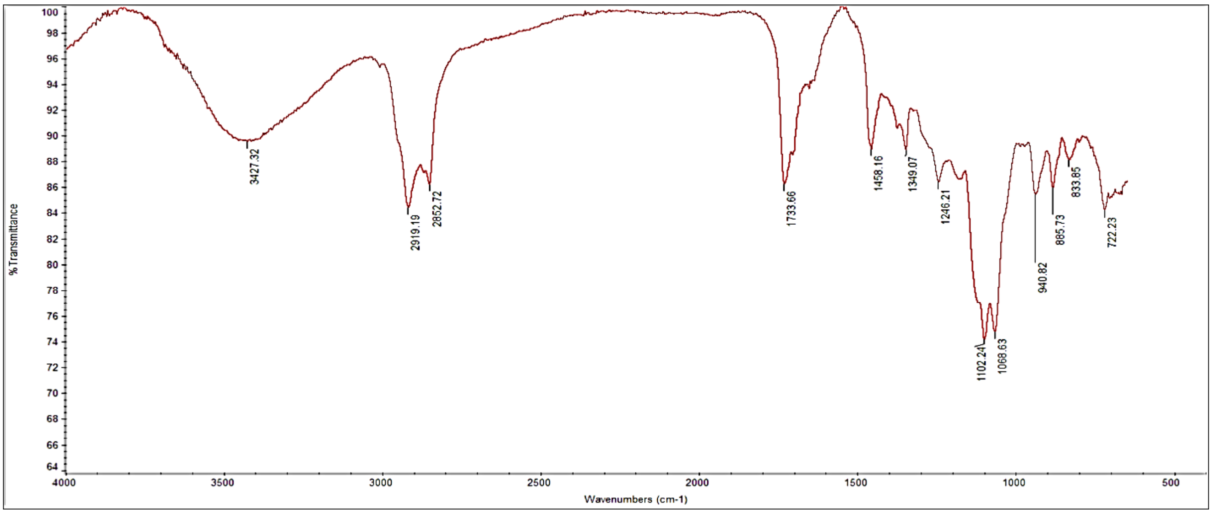


Figure-1; IR Results for ester

3.1.2. 1H NMR spectra of ester with TEG

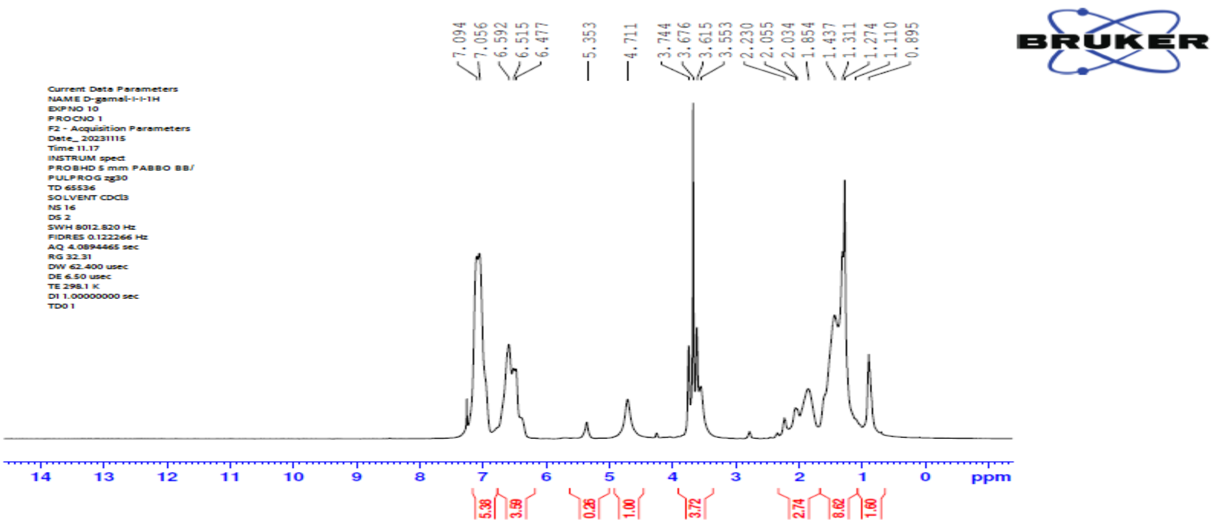


Figure-2; [1]H NMR Signals for non-ionic surfactant

1H NMR gives δ (ppm): 0.89 (t, 3H, [CH3 terminal]), 1.11 (s, 14H, [(CH2)7-chain]), 1.4 (m, 2H, [CH2CH2CH2-O-]), 2.2 (t, 2H, [-O-CO-CH2CH]), 3.7 (t, 2H, [-O-CO-CH2CH2-]).

3.2. Experimental Results:

The laboratory studies on non-ionic surfactants focused on three main areas: phase behavior, interfacial tension (IFT), and contact angle (wettability) assessments on carbonates. The surfactants utilized in this research are ethoxylated fatty acids. For the IFT and contact angle tests, a concentration of 10,000 ppm surfactant was diluted in 80,000 ppm NaCl brine.

3.2.1 Surfactant Phase Behavior:

Surfactant phase behavior is assessed to evaluate the effectiveness of the surfactant in reservoir fluids and separation times after adding the Non-ionic surfactant. Table-1, illustrates the different phase types and their descriptions. (Note, the samples of crude oil contain 10 % oil and 90% water cut), the results in table-1 are separation ratio with the time.

1- Crude oil without surfactant

2- Crude oil with surfactant (I-I), after 3 min

3- Crude oil with surfactant (I-I), after 6 min

4- Crude oil with surfactant (I-I), after 9 min

5-Crude oil with surfactant (I-I), after 20 min

Figure-3; Crude oil without and with surfactant.

Time	3 min	6 min	9 min	20 min
Separation Ratio	92%	94%	96%	99 %

Table-1; (Crude Oil Separation Time).

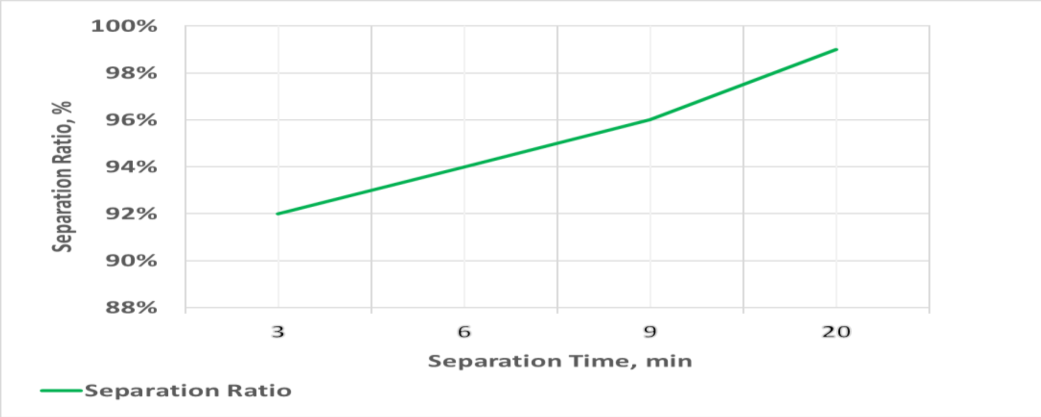


Figure-4; Crude Oil Separation Ratio with time.

3.2.3. Contact Angle Measurements:

Surfactants are after the wettability of surfaces from oil-wet to less oil-wet due to their ability to reduce surface tension. Contact angle measurements provide valuable insights into the wettability characteristics of rock surfaces. The wettability of a rock depends on various factors, including the rock type and the interactions between the surfactant and the surface. The non-ionic surfactant used in the contact angle measurements demonstrated a significant alteration in wettability with an increase in temperature. A further reduction in the contact angle was observed, leading to a transition toward water-wet conditions [29]. Although the non-ionic surfactant did not achieve the same level of water wettability as anionic surfactants, it still displayed favorable wettability values.

Temperature	25 °C		50 °C		75 °C	
Contact Angle	122.7°	123°	106.9°	106.3°	64.6°	66.6°

Table-2; Contact angle measurements.

4. CONCLUSION:

To sum up, the use of oily wastes to produce nonionic surfactants has become increasingly popular because of their sustainable and environmentally friendly characteristics. By utilizing these oil wastes, the production of nonionic surfactants can help reduce the negative environmental effects typically associated with petroleum-based surfactants. The synthesized nonionic surfactants have demonstrated exceptional surface-active properties, making them suitable for successful surfactant flooding, the strategic placement of injection and production wells is crucial to maximize oil recovery and increasing oil production.

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