Synthesis and evaluation of some polymeric surfactants for treating crude oil emulsions
Part I: treatment of sandy soil polluted with crude oil by monomeric and polymeric surfactants

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Abstract

In the present work, five surfactants were prepared; two of them were monomeric surfactants, one was anionic (triethanol ammonium salt of dodecyl benzene sulfonic acid, E1) and the second was non-ionic surfactant (nonyl phenol ethoxylate, E2). The other three surfactants were polymeric non-ionic surfactants (ethoxylated polynonyl phenol formaldehydeno-ethanol amine E3, ethoxylated poly nonyl phenol formaldehyde diethanol amine E4 and ethoxylated nonoyl phenol formaldehyde triethanol amine E5). The gel permeation chromatography (GPC) and the elemental analysis were carried out to determine the molecular weight of the polymeric surfactants. The surface properties for these surfactants were determined by measuring the surface tension, the interfacial tension, the foaming power, cloud point and the emulsification power. The polymeric surfactants were used to treat the polluted sandy soil, which saturated with two types of crude oils (waxy and asphaltinic). From the data obtained it was found that, the increasing of surfactant concentrations led to increase the reclaimation of the waxy and asphaltinic crude oil percentages and decreased the interfacial tension. The reclaimed oil percentage increased with decreasing the hydrophilic-lipophilic balance (HLB) value of non-ionic surfactant. In general behavior, the reclaimation of the asphaltenic crude oil was greater than the reclaimation of the waxy crude oil. The data were discussed on light of the chemical structure of the surfactants and composition of crude oil.

Keywords: Surfactants; Polymeric surfactants; Surface tension; Structure–property relations; Pollution; Water-soluble polymers; Clean environment

1. Introduction

The procedure selected to contain spills on land will vary with the amount and type of oil spilled, the type of soil and the terrain. Less viscous oil and
more porous soil will allow greater and more rapid penetration and lateral migration in the soil. The larger spills may require containment techniques such as digging interceptor trenches or collecting pools from which the oil may be pumped. The anionic and non-ionic surfactants were selected to wash three different soils contaminated with petroleum hydrocarbons [1].

Some studies dealt with the simulation of soil washing with surfactants, the primary objective was identification of the contributions of the various mechanisms—water displacement, surfactant mobilization and dissolution on the removal of organic contaminants from soil [2].

A study of surfactant use for remediation of organic and metal contaminated soils by surfactant sorption to soil, and treat ability for a sandy soil artificially contaminated with lead and naphthalene, has been reported [3]. The sorption of non-ionic surfactants to the soil was not affected by pH, while sorption of anionic surfactants increased as the pH decreased. The non ionic surfactants show better solubility enhancement for naphthalene than anionic surfactants, the anionic surfactant may enhance lead desorption from the soil due to the interactions between the anionic head group of the surfactant and Pb\(^{+2}\) ion. A study on in situ remediation of oil contaminated soils with surfactants via a surfactant flooding technique for the remediation of soils contaminated by semi volatile and non volatile petroleum products, such as crude and diesel oils, consist of injecting a surfactant slug into contaminated areas to mobilize oil trapped in both vadose (unsaturated) and capillary-fringe zones, and of depleting the ground water level to collect this oil. The diesel oil and surfactants were removed on site before sewage disposal by centrifuging, precipitation and finally by biodegradation [4]. The abiotic experiments results indicated that the addition of non-ionic surfactant to soil/water system increase the desorption of polyaromatic hydrocarbon (PAH) compounds, it was also observed that the desorption rate of poly-aromatic hydrocarbon compounds depend on their molecular weight. The three and four ring PAH compounds showed higher and faster desorption rates than the five and six ring PAHs [5–7]. A study on the micro emulsification approach for removing organolead and gasoline from contaminated soil was investigated [8]. The effect of an anionic surfactant on the mobilization and biodegradation of PAHs-contaminated soil was performed by using sodium dodecyl sulphate, and it has been found that, the SDS was effective in mobilizing three and four ring PAHs [9]. In the assessment of selected surfactants for enhancing carbon mineralization of an oily waste, it was found that both an anionic surfactant mixture of mono- and di-organo phosphate ester and a nonionic ethoxylated alkyl phenol ester are effective in enhancing carbon waste carbon mineralization rates (CMR) through emulsification [10]. The utilization of chemical enhanced oil recovery technology to remove hazardous oily waste from alluvium was performed by a variety of alkali plus surfactant [11]. The concentrations that are sub CMC levels of nonionic surfactant can enhance the apparent aqueous phase HOC solubility, increase the soil organic carbon content due to surfactant sorption, and modify the value of the HOC soil/aqueous distribution coefficient. This method was proposed to predict the distribution of HOC between soil and bulk solution with sub CMC aqueous phase concentration of nonionic surfactant [12]. The present study aims to synthesize five different surfactants (E\(_1\), E\(_2\), E\(_3\), E\(_4\) and E\(_5\)) and use them to treat the crude oil-polluted sandy soil by formation oil-in-water emulsion. In this respect, two Egyptian crude oils (Asphaltenic and waxy) were submitted from Qarun Petroleum Company to use them in this study.

2. Experimental

2.1. Crude oil types

Two types of crude oil were supplied from Qarun Petroleum Company (asphaltenic and waxy crude oil). Their general physicochemical properties are shown in Table 1.
2.2. Preparation of nonyl phenol

2.2.1. Acylation

A solution of nonoyl chloride (0.1 mol) was added gradually to a cold suspension of anhydrous aluminium chloride (0.4 mol) in a large excess dry phenol (200 ml). The mixture was stirred at room temperature for 8 h, and then poured in (ice–HCl) mixture. The organic layer was separated and dried with anhydrous Mg SO₄ over night, and then the mixture was distilled off to obtain the nonoyl phenol (acyl phenol) [13,14].

2.2.2. Reduction of the acyl phenol

The nonoyl phenol was reduced according to Hung-Minlon modification of Wolff–Kishner reduction to obtain the corresponding alkyl phenol (nonyl phenol). A mixture of the nonoyl phenol (0.1 mol), diethylene glycol (100 ml), hydrazine hydrate (10 ml 90%) and KOH (0.3 mol) were heated under reflux for 6 h, then poured into water and the upper organic layer was separated, then was dried over anhydrous MgSO₄.

2.3. Preparation of the polymeric and monomeric nonionic surfactants

2.3.1. Polymerization

Three polymeric surfactants (E₂₋₅) were prepared as; (1 mol) nonyl phenol, (1.2 mol) p-formaldehyde and (1 mol) of mono- or di-or triethanol amine were placed in a 1 l flask with four necks, fitted with a condenser, a mechanical stirrer, a thermometer and a dropping funnel. An amount of the concentrated HCl equivalent to 2% of the total weight of the reactants was placed in the dropping funnel. The HCl was added drop wise with continuous stirring over a period of 1 h, and the temperature is maintained at 35 °C. The temperature raised gradually by means of a heating jacket to 110 °C for 1 h. A Dean Stark water collector was then attached to the reactor and connected to a vacuum pump adjusted to 50 mm Hg. The temperature was raised to 150 °C. The reactants were allowed to stand at this temperature for another 1 h. The product was then cooled and dissolved in benzene, then washed with 10% sodium carbonate solution until neutralization had been reached and then dried after separation of the aqueous phase. The benzene was then removed by means of a rotary evaporator to get the polyalkylphenol formaldehyde alkanol amine resin [15]. The molecular weights were determined by gel permeation chromatography (GPC) analysis by using high performance liquid chromatography (HPLC; model Waters 600 E, Germany) and the Nitrogen content was determined by using the Elemintal Analysis (model 240 B, USA) Table 2.

2.3.2. Ethoxylation

Ethoxylation of the hydroxyl group of nonyl phenol or polyalkylphenol formaldehyde amine resins was achieved by condensing (1 mol) of either of them with (n mol) of ethylene oxide in the presence of Na-metal as a catalyst, in nitrogen flushed system at 180 °C, followed by neutralization for the catalyst by HCl. Dissolve the product

<table>
<thead>
<tr>
<th>Specification</th>
<th>Method</th>
<th>Asphaltene crude oil</th>
<th>Waxy crude oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>API gravity at 60 °F</td>
<td>IP160</td>
<td>27.1</td>
<td>42.6</td>
</tr>
<tr>
<td>Kinematics viscosity at 60 °F (c St)</td>
<td>IP160</td>
<td>13.9</td>
<td>2.5</td>
</tr>
<tr>
<td>Reid vapor pressure, (PSI)</td>
<td>IP 71</td>
<td>3.2</td>
<td>8</td>
</tr>
<tr>
<td>Asphaltenes and resins (wt.%)</td>
<td>IP 143</td>
<td>6.8</td>
<td>1.5</td>
</tr>
<tr>
<td>Sulphur contents (wt.%)</td>
<td>UOP 46</td>
<td>1.4</td>
<td>0.01</td>
</tr>
<tr>
<td>Water content, (wt.%)</td>
<td>IP 74/80</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Crude oil–distilled water IFT, (mN m⁻¹) at 25 °C</td>
<td>–</td>
<td>18.0</td>
<td>14.6</td>
</tr>
<tr>
<td>Wax content (wt.%)</td>
<td>UO P46/85</td>
<td>1.6</td>
<td>16.5</td>
</tr>
<tr>
<td>Salt content (wt.%)</td>
<td>ASTM D3230</td>
<td>35 PTB</td>
<td>10 PTB</td>
</tr>
</tbody>
</table>

Table 1
Physicochemical properties of the used crude oils

Table 2
The general characters of the prepared surfactants

<table>
<thead>
<tr>
<th>Surfactants</th>
<th>Molecular weight before ethoxyl-ation</th>
<th>Molecular weight after ethoxyl-ation</th>
<th>Nitrogen content (%)</th>
<th>Foaming height (cm)</th>
<th>Cloud point (°C)</th>
<th>Emulsification stability (h:min)</th>
<th>HLB</th>
</tr>
</thead>
<tbody>
<tr>
<td>E1</td>
<td>480</td>
<td>-</td>
<td>2.92</td>
<td>25.5</td>
<td>–</td>
<td>0:32</td>
<td>23.8</td>
</tr>
<tr>
<td>E2</td>
<td>220</td>
<td>704, e.o. = 11</td>
<td>–</td>
<td>19.0</td>
<td>58–60</td>
<td>1:32</td>
<td>13.8</td>
</tr>
<tr>
<td>E3</td>
<td>5220</td>
<td>11204, e.o. = 136</td>
<td>4.82</td>
<td>13.0</td>
<td>68–70</td>
<td>2:00</td>
<td>10.7</td>
</tr>
<tr>
<td>E4</td>
<td>1702</td>
<td>3373, e.o. = 37</td>
<td>4.93</td>
<td>15.5</td>
<td>66–68</td>
<td>6:00</td>
<td>9.7</td>
</tr>
<tr>
<td>E5</td>
<td>1095</td>
<td>2032, e.o. = 21.3</td>
<td>5.11</td>
<td>17.4</td>
<td>64–66</td>
<td>24:00</td>
<td>9.2</td>
</tr>
</tbody>
</table>
in isopropanol, then the mixture was heated in aqueous super saturated NaCl solution at 90 °C with continuous stirring for 1 h. The organic layer was separated, and then isopropanol was distilled off. The product was dried and collected. The generalized formula for these surfactants are shown in Fig. 1.

2.3.3. Preparation of the triethanolamonium salt of dodecyl benzene sulpheric acid (E₁)

One (mol) of dodecyl benzene sulpheric acid and (1 mol) of triethanolamine were reacted in 250 ml one necked flask fitted with condenser and stirring at 80 °C to prepare their corresponding ammonium salt after complete neutralization. The product was dissolved in ethyl alcohol, to precipitate the ammonium salt, and was then made decantation followed with drying [16].

2.3.4. Foaming power measurements

The foam height was measured as the Ross–Miles method [17]. 200 ml of a solution of surfactant (1% conc.) contained in a pipette of specified dimensions with a 2.9 mm internal diameter, from the orifice 90 cm are allowed to fall onto 50 ml of same solution contained in a cylindrical vessel maintained at a given temperature (60 °C) by means of a water jacket. The height of the foam produced in the cylindrical vessel was read immediately after all the solution had run out of the pipette (initial foam height) and again after a given amount of time (generally 5 min).

2.3.5. Cloud point measurements

It was measured as described before [18], it was marked by the aggregation of the dehydrated micelles into layer aggregates at certain temperature. Diffusion of the surfactant molecules from these aggregated micelle to the newly created interfaces involved in bubble formation might be much slower than from the more highly hydrated smaller micelle. Thus decreasing the stabilization of the liquid lamella in the formed foam.

2.3.6. Emulsification power measurement

The efficiency of the prepared surfactants was determined for water-in-oil emulsions (w/o). It is of interest to mention that the prepared surfactants were found to be soluble in both water and xylene. A mixture of 10 ml deionized water (0.1 gm surfactant concentration) and 5 ml of xylene. The test tube containing the mixture was shaken vigorously for 1 min and was then allowed to seal. The emulsion stability was taken as the time for separation of 9 ml of the aqueous phase [19].

2.4. Cleaning of the oily polluted sandy soil process

A sample (200 g) of sandy soil has particle size 80 μm, was saturated by (5 ml) asphaltenic or waxy crude oil. The oil saturated sandy soil sample was placed in a central glass funnel size G1. The funnel was fitted on Buchner conical glass, which connected, with Dosen circulation pump. The different surfactant (emulsifier) concentrations (0.25, 0.5, 1, 3 and 5%) were freshly prepared in 200 ml tap water. The vacuum was turned on and the surfactant solution was added to the polluted sample in the funnel. The suction and recirculation were carried out for 2 h. The effluent was collected in form of oil-in-water emulsion, then 100 ml of chloroform was added to the collected emulsion to extract the emulsified crude oil by vigorous agitation. The organic layer (lower) was separated by using separating funnel. The efficiency of surfactants to clean and emulsify the crude oil from the surface of the sand sample was determined by colorimetric method using spectrophotometer model, ANA Number 4205, Japan [20].

3. Results and discussion

3.1. Effect of ethanolamine type on the degree of polymerization

The prepared polymeric surfactants (E₃, E₄, and E₅) were based on changing of the alkanolamine (monoelthanol, diethanol or triethanol amine) in the structure of the polymer. The molecular weights were determined by using, the ‘GPC’. The molecular weights of E₃, E₄ and E₅ were 5220, 1702 and 1095, respectively, before the ethoxylation process. From the data of molecular weight, it may be concluded that, the type of
ethanolamine plays a central role in the built up of the polymer skeleton. This means that the mono-ethanolamine is more reactive among di-or tri-ethanolamine in the polymerization process, this reactivity ranked the molecular weight in this order $E_3 > E_4 > E_5$, respectively.
3.2. Foaming power (FP)

In general the nonionic surfactants form unstable foams. The nonionic surfactants show foam volume and foam stability smaller than the ionic surfactants in aqueous medium, due to the larger surface area per molecule and the absence of highly charged films in these foams. In ethoxylated nonionic surfactants both the foam stability and foam volume reach a maximum at a particular ethylene oxide units [21]. This is ascribed to a maximum in intermolecular cohesive forces in the adsorbed film as the ethylene oxide content increases. The data of foaming power in Table 2 show that, the foam stability increases with decreasing of the ethylene oxide units for the surfactants E3, E4 and E5. The foam stability for these polymeric surfactants was ranked as: E5 > E4 > E3 (17.4, 15.5 and 13.0 cm, respectively), these results are in consistency with the data reported else where [22]. The nonionic surfactant E2 (nonylphenol ethoxylate) exhibited 17.5 cm foam height, but the ionic emulsifier E1 (triethanol ammonium salt of dodecyl benzene sulfonic acid) exhibited 25.5 cm foam height, this means that the ionic surfactants have highly charged surface film on their foams, leads to increase its height and stability. It can be concluded that, the surfactant, which has the lowest foam height and the lowest foam stability, has a good detergency power as reported before [23].

3.3. Cloud point

The cloud point is a measure of the inverse solubility characteristic of non-ionic surfactant. The energy of the hydrogen bond is insufficient to retain the surfactant molecules and the dehydration takes place when the surfactant solution is heated at elevated temperature, and the most of surfactants molecules separate out with little amount of water. The surfactant solubility in water at certain temperature shows turbidity by heating. This turbidity is reversible, so that the solution clears again on cooling [24–26]. The data presented in Table 2 reveal that, the cloud point increases with increasing of ethylene oxide units [27]. From these data, it may be concluded that the cloud point of the monomeric non-ionic surfactant E2 is less than non-ionic polymeric surfactants (E3, E4 or E5). The cloud points were (58–60 °C), (68–70 °C), (66–68 °C) and (64–66 °C), respectively, for the surfactants E2, E3, E4 and E5.

3.4. Emulsification power and HLB

The data in Table 2 reveal that, the surfactant E5 exhibited the maximum emulsion stability (24 h), but the E1 exhibited the minimum emulsion stability (0:32 h). The order of emulsion stability can be ranked as follows: E5 > E4 > E3 > E2 > E1. This behavior may be due to the presence of a large difference between their hydrophilic–lipophilic balance (HLBs). The HLB of E1 (23.8) leads to increase its solubility in water by ionic solubility and decreases its affinity to form a stable emulsion [28]. Meanwhile the HLB of E5 is (9.2), this means that, its solubility in water is more less than E1 because the former (E5) solubles in water by solvation so that it gave the highest emulsion stability. From the data presented in Table 2 it can be concluded that, there is an inverse relationship between the emulsion stability and the HLB of the surfactant.

3.5. Treatment the polluted sandy soil by surfactants

The aqueous solution of the investigated surfactants E1–E5 in different concentrations were added to the polluted sandy soil by waxy or asphaltenic crude oil. This process was carried out to clean the adsorbed oil from the surface of the sand in form of oil-in-water emulsion (o/w). The clean up of the sand sample was depending on surfactant concentration, surfactant type, HLB of surfactant, interfacial tension and the composition of crude oil.

3.6. Effect of surfactant concentration on reclamation of the adsorbed crude oil on the sand surface

The data in Fig. 2 reveal that, the increasing of surfactant concentration was accompanying with increasing of the reclamation of waxy crude oil.
percentage. This behavior was a general pattern for the surfactants E₁–E₅. By inspection the data in Fig. 2, it has been found that, the anionic surfactant E₁ exhibited the maximum efficiency to reclaim the oil in all concentrations, if it was compared with both the non-ionic monomeric surfactant (E₂) and the other polymeric surfactants (E₃, E₄ or E₅). On the other hand, the monomeric surfactant (E₂) pronounced a greater reclamation of waxy crude oil percentage than which exhibited with the polymeric surfactants (E₃, E₄ or E₅). The reversible behavior has been seen for the reclamation of asphaltenic crude oil from the polluted sandy soil as clear from the data in Fig. 3. The show of Fig. 3 reveals that, the relation between surfactant concentration and the percentage of the reclaimed asphaltenic crude oil. By comparison the data of Figs. 2 and 3, it can be concluded that, the surfactant E₁ and E₅ are more efficient to remove the asphaltenic crude oil than the waxy crude oil from the surface of the sandy soil. This behavior may be due to the presence of aromatic ring in the skeleton of the surfactant structure which may be lead to increase the compatibility of the surfactant with the asphaltenic crude oil components (resin, aromatic and asphaltenite) which lead to increase the oil solubility to form oil in water emulsion (o/w), in the cleaning process.

3.7. The relevance HLB of reclaimed oil percentage

The HLB of surfactant changes systematically by changing the number of ethylene oxide units in the case of non-ionic surfactant [29]. The values of HLBS for E₂, E₃, E₄, and E₅ were 13.8, 10.7, 9.7 and 9.2, respectively, as listed in Table 2. The Figs. 4 and 5 show the relation between HLB of non-ionic surfactant and the reclamation of the asphaltenic and the waxy crude oil percentages. In Fig. 4, for the asphaltenic crude oil, it was found that, the reclaimed oil percentage increases with decreasing the HLB of the surfactant. The plots in Fig. 5 clear the relation between HLB of the non-ionic surfactants (E₂, E₃, E₄ or E₅) and the reclamation oil percentage of the waxy crude oil. It can be concluded that, the reclamation of the oil percentage increases with increasing the HLB of surfactant. This behavior may be due to the crude oil compositions play important role of the total reclamation oil percentage. Meanwhile in the instance of the asphaltenic crude oil, the increasing
of asphaltene content may be considered the main reason which makes the crude oil more compatible with the lowest HLB surfactant. On the other hand the reclamation oil percentage of the waxy crude oil increased with increasing the HLB of surfactant. This means that the increasing of wax content in the waxy crude oil increases its compatibility with the surfactants, which have the highest HLB values.

3.8. The role of IFT in emulsion stability of waxy and asphaltenic crude oils

In general pattern, the increasing of surfactant concentration reduces the interfacial tension. In Fig. 6 the surfactant concentration was plotted against the interfacial tension for the waxy crude oil and Fig. 7 for the asphaltenic crude oil. The increasing of surfactant concentration may increase the adsorption of surfactant molecules on the oil-in-water interface. The adsorption of surfactant molecules on the interface minimizes the interfacial tension between the water and oil, which leads to form a stable (o/w) emulsion [30]. The interfacial tension is regarded as a factor playing a crucial role in emulsion stability [31]. The low interfacial tension is necessary for emulsion formation, but it is not the only factor for emulsion stability [32]. The monomeric non-ionic surfactant E2 (nonyl phenol ethoxylate e.o. = 11) exhibited greater reduction of interfacial tension than the polymeric surfactants (E3, E4 or E5), this may be due to the aggregation of the monomeric surfactant molecules on the interface was greater than the polymeric surfactants, which leads to minimize the interfacial tension. The more reduction of the interfacial tension, which obtained with E1 (anionic surfactant) against the waxy and asphaltenic crude oils, strongly helped to emulsify the crude oil which adsorbed on the sand, comparing with non-ionic monomeric surfactant E2 and the polymeric surfactants (E3, E4 or E5). This may be due to the solubility of the anionic surfactant (E1) depends on the ionic strength of the surfactant molecules which increased the affinity of the crude oil to form o/w emulsion. It was found that, the IFT values for the fifth surfactants against waxy crude oil are more less than the values, which were obtained for the same surfactants against the asphaltenic crude oil [32]. But the
reclamation of the asphaltenic crude oil percentage was greater than the percentages that obtained with waxy crude oil. This may be due to increase of the asphaltene content which gives the highest values of the IFT, which associated with the highest emulsion stability during circulation process, but this behavior is vice versa in the case of the waxy crude oil. So that, the treatment of crude oils from the polluted sandy soil, the maximum solubilization and emulsification of the oil was obtained at concentrations of the surfactant considerably above the critical micelle concentration [33]. From the results obtained, it has been concluded that, their is a direct relation between the reclaimation oil percentage by surfactant and foam stability, but indirect relation with emulsion stability.

4. Conclusion

The conclusion of this work can be drawn in the following points:

1) The ethanolamine play a central role in the built up of the polymer skeleton.
2) The ionic surfactants have highly charged surface film on their foams, leading to increase the foam height and its stability.
3) The cloud point increases with increasing of ethylene oxide units.
4) The surfactant E₅ exhibited the maximum emulsion stability but the E₁ exhibited the minimum emulsion stability.
5) The increasing of surfactant concentration reduces the interfacial tension.
6) The reclaimed oil percentage increased with decreasing the HLB value of surfactant.
7) The anionic surfactant E₁ exhibited the maximum efficiency of the reclaimation process if it was compared with both the non-ionic monomeric surfactant E₂ and the other polymeric surfactants (E₃, E₄ or E₅). The surfac-
tants E₁ and E₅ were the most efficient to clean the asphaltenic than the waxy crude oil from the surface of polluted sandy soil.

References