Synthesis and Performance of Glycerol Ester-Based Nonionic Surfactants

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ABSTRACT

A series of novel glycerol-based nonionic surfactants were synthesized from the trans esterification of various long chain fatty acid methyl ester with glycerol ester of dibasic acid (succinic acid, and adipic acid). The chemical structure of the prepared compounds was confirmed using elemental analysis, FTIR and $^1$H-NMR spectroscopy. Surface active properties at air-aqueous solution were determined using Gibb’s adsorption equations including critical micelle concentration (cmc), surface excess at air water interface ($\Gamma_{\text{max}}$) and minimum surface area ($A_{\text{min}}$). The effects of hydrophobic and hydrophilic chain length on the surface parameters of the prepared surfactants were discussed. Surfactants with proper HLB which were soluble in the oil phase and in the presence of a very small amount of water formed a stable emulsion. The solubility state of oil and surfactant was the key to making a fine emulsion.

Keywords: Surface activity, Critical micelle concentration, emulsification properties, glyceryl ester, nonionic surfactants.

INTRODUCTION

Today, new surfactants should be milder, safer and efficient, with a minimal impact upon the environment. Since glycerol derived ester-based surfactants present excellent ecological and toxicological properties and interesting interfacial behavior, they received specific attention. Due to the presence of specific hydrophilic and hydrophobic moieties in their structures, they act as important non-ionic surfactants of low HLB value, especially valuable as benign and environmentally friendly ‘‘water in oil’’ emulsifiers [1].

Recent studies can be found in the literature concerning glycerol monofatty esters (monoglycerides), synthesis [2,3]. This type of esters (monoglycerides), is widely used in a variety of industries such as food and feed production [4], cosmetics [5] pharmaceutical formulations [6] topical drug delivery systems [7] oil well drilling [8] textile [9], packaging [10] plastic processing [11] and construction materials [12]. They act as emulsifiers, emollients, lubricants and dispersants.
The synthesis of two diglycerides (1,3-dioleoyl and 1,3-distearoyl ester) molecules linked together with a short chain dibasic acid (fumaric, succinic, and adipic acid) at position 2 was reported [13]. These esters can be edible and digestible since fumaric and succinic acids occur as metabolites in the Krebs cycle for the metabolism of fats. In addition, this synthetic ester [bis-(glycerol 1,3-distearate) succinate] possesses lubrication properties [14]. Mono- and di-esterified glycerol esters which are useful for the synthesis of biodegradable polymers and surfactants were synthesized from the enzymatic esterification of glycerol with adipic, sebacic acids, and their dimethylester derivatives [15].

The synthesis of oligoesters from oxalic acid and glycerol was reported by Alksnis and colleagues [16]. Trans esterification of glycerol with dicarboxylic acid esters (C₂–C₉) was described by Gladys et al. [17]. New set of glycerol-derived oligomers solubilized from cork suberin was reported by Graca and Santos [18]. Polyester films, which are useful in surface coatings industries, were synthesized from glycerol with different chain lengths of aliphatic and aromatic dicarboxylic acids [19, 20]. However, the synthesis of glycerol with short carbon chain dicarboxylic acid esters was limited. So, this work is considered as an addition to this subject.

The main objective of this work was to prepare a series of nonionic surfactants based on glycerol ester of dibasic acid (succinic and adipic acid) and fatty methyl ester (myristate, palmitate and stearate ester). These surfactants are tested for their surface tension reduction and emulsion stabilizing capability. The effects of the hydrophilic and hydrophobic moieties on their physicochemical properties are also studied.

**MATERIALS AND METHODS**

**Materials.**
The fatty acids, myristic, palmitic and stearic acids were purchased from Prolabo laboratory chemicals analytical grade purity 99%. Glycerol, from Sigma product with purity >99% was used without further purification. The dibasic acids (succinic and adipic acid), sulphuric and P-toluene sulfonic acids were purchased from Aldrich. All solvents used throughout this study were of the chemically pure grade and were fractionally distilled just before use. The water used in the surfactant tests was purified by water purification system.

**Apparatus:**. Infrared (IR) spectra were obtained on 1600 FTIR Perkin Elmer-Spectrum in the 400–4,000 cm⁻¹ range using KBr pellets.¹H nuclear magnetic resonance (¹HNMR) spectra were obtained with Varian 300 MHz spectrometer with TMS as an internal standard.

**Synthesis.** The structure of the synthesized compounds are shown in the following Scheme:-

2.1- **Synthesis of bis (2,3- dihydroxypropyl ) succinate I₂ ; bis (2,3- dihydroxypropyl) adipate I₄.**
Esterification was performed in a 250-mL three-necked flask equipped with a reflux condenser, thermometer, and a sampling port. The flask was heated to 80°C in a water bath, and its contents were stirred magnetically. The reagents used were in a molar ratio, 4 mol of glycerol to 1 mol of succinic acid; the reaction was catalyzed by 0.1% w/w H₂SO₄ (of total). On completion of the reaction, the reaction mixture was washed with water and the glycerol ester extracted with Chloroform. Analogous synthetic procedures were performed for the synthesis of bis (2,3-dihydroxypropyl) adipate. The products were analyzed directly, by acid value, hydroxyl value and saponification value. IR (KBr, cm⁻¹): 3380 (OH), 2943 (CH₂)n, 2888 (CH₂)n, 1731(CO),
H NMR assignments are quite similar for the different esters \((\text{CH}_2)_n(\text{COOCH}_2\text{CHOHCH}_2\text{OH})_2\) and are only given for the \((\text{CH}_2)_2(\text{COOCH}_2\text{CHOHCH}_2\text{OH})_2\) I: δ 2(S, 4H, (OH)_{4}), 2.4(S,4H,CH_{2}-C=O)_{2}), 3.56 -3.81(m,4H,CH_{2}OH)_{2}, 3.9 (m, 2H, (CH OH)_{2} ) 4.11-4.36 (m, 6H,( CH_{2}-O)_{3}).

Elemental analysis: I 2. Calcd. for C_{10}H_{18}O_{8}: C, 45.11; H, 6.77; O, 48.12. Found: C, 44.93; H, 6.56; O, 47.98%. I 4 Calcd. for C_{12}H_{22}O_{8}: C, 48.98; H, 7.48; O, 43.54. Found: C, 48.74; H, 7.28; O, 43.13%.

Scheme 1 Synthetic routes for the preparation of nonionic surfactants.

2.2- Synthesis of 3-acyloxy-2-hydroxypropyl 2,3-dihydroxypropyl succinate II2a-c; 3-acyloxy-2-hydroxypropyl 2,3-dihydroxypropyl adipate II4a-c; bis (3-acyloxy-2-hydroxypropyl) succinate III2a-c; bis (3-acyloxy-2-hydroxypropyl) adipate III4a-c.

The methyl esters of the different fatty acids were prepared according to the method reported by Bondiol [21] and they were used in the following preparation.

Bis(2,3- dihydroxypropyl) succinate was dissolved in 50 ml dimethyl formamide in a 250 ml Erlenmeyer flask, then stirred with methylester (myristate, palmitate, stearate) in 1:1 and 1:2 molar ratios in presence of 0.1% w/w H_2SO_4 (of total). The mixture was heated under reflux for 6 hr. Dimethyl formamide was removed by distillation. The product was dissolved in acetone and the solution was cooled in refrigerator, then filtered through filter paper. Analogous
synthetic procedures were performed for the synthesis of 3-acyloxy-2-hydroxypropyl 2,3-dihydroxypropyl succinate, adipate (IIa-c), (IIIa-c). The products were characterized IR (KBr, cm$^{-1}$) for selected compound (IIb) (KBr, cm$^{-1}$): 3394 (OH), 2927 (CH$_2$)$n$, 2854(CH$_2$)$_n$, 1736(CO), and $^1$H-NMR spectroscopy: $\delta$ 0.96 ($t$, 3H, -CH$_3$), 1.29 ($m$, 14H, -(CH$_2$)$_2$), 1.33 (m, 2H, CH$_2$, -OH), 1.68 ($m$, 6H, CO, CH$_2$(CH$_2$)$_3$), 2.63 ($s$, 3H, (OH)$_3$), 2.25 (m, 6H, (CH$_2$ -C=O)), 3.56 -3.81 (m, 2H, CH$_2$OH), 4.11 - 4.36 ($m$, 2H, (CH OH)$_2$), 4.41 ($m$, 6H, (CH$_2$-O)$_3$).

Hydroxyl and saponification value were determined by the AOCS method$^{(13,15)}$. Acid value test method covers the measurement of the free acidity of compounds by the reaction with standard alkali solution$^{(14)}$. Duplicate analyses were performed for each sample, and the mean value was reported.

2.3- Evaluation Methods of Surface Active Properties

2.3.1- Surface Tension ($\gamma$) and Critical Micelle Concentration (CMC)

The surface tension $\gamma$ of different concentrations of glycerol-based nonionic surfactants (II$_{2a}$-III$_{4c}$) was continuously recorded for 15 min. using a semiautomatic tensiometer apparatus (Krüss K10 Tensiometer) by Du Nouy platinum ring method. The relation between the surface tension and the concentration (in term of log $c$) of the synthesized surfactants at 25 $^\circ$C was determined and represented in (Fig.1,2). The CMC and $\gamma_{\text{CMC}}$ (surface tension at CMC) values were determined from the break point of each surface tension versus concentration.

![Fig. 1 Surface tension versus logarithm of concentration, $c$, for surfactants II$_{2a}$-II$_{4c}$ at 25 $^\circ$C](image)

2.3.2-Maximum Surface Excess ($\Gamma_{\text{max}}$).

The maximum surface excess of the surfactant solution ($\Gamma_{\text{max}}$) is defined as the concentration of the surfactant molecules at the interface near the CMC [22].

$$\Gamma_{\text{max}} = \frac{1.2.303RT(\delta\gamma/\delta\log C)}{T}$$

where $R = 8.314$ J mol$^{-1}$ K$^{-1}$, $T$ is the absolute temperature and $(\delta\gamma/\delta\log c)$ is the slope of the $\gamma$ versus log $c$ plot at room temperature (Fig. 1,2).
Fig. 2 Surface tension versus logarithm of concentration, c, for surfactants III2a-III4c at 25 ºC

2.3.3 Minimum Surface Area (A$_{\text{min}}$).
The minimum surface area A$_{\text{min}}$ is the minimum area per molecule of the prepared compounds at the interface and was calculated using the following equation:

$$A_{\text{min}} = 10^{14} / N \Gamma_{\text{max}}$$

where $N$ is Avogadro’s number and $\Gamma_{\text{max}}$ is the maximum surface excess.

2.3.4 -The Standard Free Energy of Micellization ($\Delta G_{\text{mic}}$)
It is expected that the process of micellization occurs simultaneously. The dominance of the process is decided by the free energy changes. Hence, the free energy of micellization ($\Delta G_{\text{mic}}$) were calculated according to Rosen’s methodology [23].

$$\Delta G_{\text{mic}}^\circ = RT \ln C_{\text{CMC}}$$

2.3.5- Preparation of emulsions
water–oil type of emulsion was prepared by mixing coconut oil, surfactants, and water. Oil and water were taken in 3:1 ratio and 0.6% (by weight) of the prepared surfactants. The mixture was stirred for 30 min. at 3,000 rpm by a magnetic stirrer to prepare the emulsion.

2.3.6- Microscopic examination of the emulsions
It has been demonstrated that the optical microscope can be an alternative method for the characterization of emulsions [24]. The emulsion stability was monitored by an Olympus microscope. The images were snapped with a camera installed on the microscope at a magnification of 20 times and the diluted emulsions were observed.

2.3.7- Emulsions stability
The amount of water separated from the emulsion sample at 25°C was measured as a function of time. The stability of the W/O emulsion was defined as the emulsion preservation ratio, i.e., the volume of water that separated from the emulsion divided by the total volume of water contained in the emulsion sample.
RESULTS AND DISCUSSION

3.1- Synthesis.
The esterification of dicarboxylic acids (succinic and adipic acid) with glycerol was relatively simple and went as expected and as demonstrated in the literature [18]. The molar ratio of glycerol esters of dicarboxylic acids and methyl fatty esters were varied, with equal molar ratio one fatty acyl group from methyl fatty esters reacts with one primary alcohol of the glycerol ester of dicarboxylic acids to produce mono 3-acyloxy-2-hydroxypropyl ester of dicarboxylic acid. But when excess methyl fatty ester was used (two mole), two fatty acyl group react with primary alcohol to form bis (3-acyloxy-2-hydroxypropyl) ester of dicarboxylic acid. Scheme 1 summarizes the pathways describe the synthesis of nonionic surfactants. Physicochemical characteristics of the prepared compounds (I2-III4c) are tabulated in Table 1. The reaction progress was confirmed by determining the saponification value and hydroxyl percent of the products. The hydroxyl percent showing a decrease from ordinary glycerol (56.54%) to bis (3-acyloxy-2-hydroxypropyl) ester of dicarboxylic acid (5.31-.4.45%).

Table1 Physicochemical Characteristics for the prepared compounds( I2-III4c )

<table>
<thead>
<tr>
<th>Compound</th>
<th>Yield %</th>
<th>Molecular Formula Mol Wt</th>
<th>A.V</th>
<th>S.V</th>
<th>OH %</th>
<th>OH number</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Theo</td>
<td>exp</td>
<td>Theo</td>
<td>exp</td>
</tr>
<tr>
<td>Glycerol</td>
<td>-</td>
<td>C₆H₁₂O₃ 92</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>I₂</td>
<td>87</td>
<td>C₁₀H₁₉O₈ 266</td>
<td>- 3.6</td>
<td>421.80</td>
<td>439.50</td>
<td>25.56</td>
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<tr>
<td>I₄</td>
<td>89</td>
<td>C₁₂H₂₂O₈ 294</td>
<td>- 4.1</td>
<td>381.60</td>
<td>398.20</td>
<td>23.13</td>
</tr>
<tr>
<td>II₂a</td>
<td>87</td>
<td>C₁₀H₂₄O₉ 476</td>
<td>- 3.7</td>
<td>353.57</td>
<td>359.78</td>
<td>10.71</td>
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<td>II₂b</td>
<td>84</td>
<td>C₁₀H₂₄O₉ 504</td>
<td>- 3.3</td>
<td>333.93</td>
<td>338.67</td>
<td>10.12</td>
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<tr>
<td>II₂c</td>
<td>85</td>
<td>C₁₀H₂₄O₉ 532</td>
<td>- 4.6</td>
<td>316.35</td>
<td>322.54</td>
<td>9.59</td>
</tr>
<tr>
<td>II₄a</td>
<td>81</td>
<td>C₁₂H₃₈O₉ 504</td>
<td>- 2.5</td>
<td>333.90</td>
<td>340.11</td>
<td>10.12</td>
</tr>
<tr>
<td>II₄b</td>
<td>86</td>
<td>C₁₂H₃₈O₉ 532</td>
<td>- 2.8</td>
<td>316.35</td>
<td>320.95</td>
<td>9.59</td>
</tr>
<tr>
<td>II₄c</td>
<td>89</td>
<td>C₁₂H₅₆O₉ 560</td>
<td>- 3.2</td>
<td>300.54</td>
<td>307.62</td>
<td>9.11</td>
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<td>III₂a</td>
<td>85</td>
<td>C₁₃H₇₀O₁₀ 686</td>
<td>- 2.6</td>
<td>327.11</td>
<td>332.52</td>
<td>4.96</td>
</tr>
<tr>
<td>III₂b</td>
<td>79</td>
<td>C₁₃H₇₂O₁₀ 742</td>
<td>- 4.2</td>
<td>302.43</td>
<td>309.55</td>
<td>4.58</td>
</tr>
<tr>
<td>III₂c</td>
<td>86</td>
<td>C₁₃H₇₂O₁₀ 798</td>
<td>- 3.4</td>
<td>281.20</td>
<td>289.21</td>
<td>4.26</td>
</tr>
<tr>
<td>III₄a</td>
<td>80</td>
<td>C₁₃H₇₂O₁₀ 714</td>
<td>- 3.8</td>
<td>314.29</td>
<td>319.59</td>
<td>4.76</td>
</tr>
<tr>
<td>III₄b</td>
<td>87</td>
<td>C₁₄H₇₄O₁₀ 770</td>
<td>- 4.5</td>
<td>291.43</td>
<td>299.32</td>
<td>4.41</td>
</tr>
<tr>
<td>III₄c</td>
<td>83</td>
<td>C₁₄H₇₆O₁₀ 826</td>
<td>- 3.9</td>
<td>271.67</td>
<td>277.56</td>
<td>4.12</td>
</tr>
</tbody>
</table>

The FTIR spectrum of the glycerol ester of dicarboxylic acids was similar to that of mono 3-acyloxy-2-hydroxypropyl and bis (3-acyloxy-2-hydroxypropyl) ester of dicarboxylic acid but
the ratio of the signal of the C-H band at 2873-2933 cm\(^{-1}\) compared to the O-H signal at 3280 cm\(^{-1}\) increased significantly.\(^1\) HNMR spectra showed that, the integration ratio of (CH\(_2\))\(_m\) in fatty acyl group for compounds (III) was much higher than that for compounds (II) which confirm the presence of the two fatty acyl groups in compounds (III).

### 3.2-Surface-active properties

Plots of surface tension vs. concentration of glycerol-based nonionic surfactants (II\(2\)a -III\(4\)c) are reported in Figures 1 and 2. The surface tension of nonionic aqueous system follow the typical trend with surfactants concentration up to certain point and then at higher concentration the value of surface tension becomes almost constant. Therefore, the constant value of the surface tension at higher surfactant concentration can be attributed to the monomer saturation at the interface. The ability of these surfactants to lower surface tension (\(\gamma_{\text{cmc}}\)), critical micelle concentration (cmc), surface excess at air water interface (\(\Gamma\)), area per molecule at interface (A) and standard free energy of micellization (\(\Delta G_{\text{mic}}\)) are summarized in Table 2 along with reference data for previously reported nonionic surfactants\([25]\). The cmc values, which were between 6.31x10\(^{-3}\) and 5.01x10\(^{-5}\) mM, decrease with increases in the hydrocarbon chain length in both homologous series, while \(\gamma_{\text{cmc}}\) values vary in the opposite way and rise from 26.0 to 37.5 mN/m. The presence of the two acyl groups attached to the primary alcohols of glycerol decreases the cmc, for compounds (III\(2\)a– III\(4\)c).

![Optical microscopic photographs of emulsion droplets prepared using coconut oil](image-url)
**Table 2** Surface Tension at(cmc), Critical Micelle Concentration (cmc), Maximum Surface Excess Concentration(Гmax), Minimum Area/Molecule (A²), Standard Free Energy of Micellization (ΔΔGmic) at the liquid /air interface and emulsion stability % at 25 ºC of glycerol-based nonionic surfactants (II2a-III4c)

<table>
<thead>
<tr>
<th>Surfactants a</th>
<th>Г cmc mN/m</th>
<th>cmc mol/l</th>
<th>Гmax x10² mol/cm²</th>
<th>Area mol⁻¹ A²</th>
<th>ΔΔGmic° kJ/mol</th>
<th>HLB</th>
<th>W/O emulsion stability (%) 4hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>II2a</td>
<td>26.0</td>
<td>6.31x10⁻³</td>
<td>3.40</td>
<td>48.80</td>
<td>-12.33</td>
<td>7.68</td>
<td>75</td>
</tr>
<tr>
<td>II2b</td>
<td>27.0</td>
<td>3.02x10⁻³</td>
<td>2.89</td>
<td>57.40</td>
<td>-14.13</td>
<td>7.26</td>
<td>90</td>
</tr>
<tr>
<td>II2c</td>
<td>28.3</td>
<td>1.77 x10⁻³</td>
<td>2.55</td>
<td>65.11</td>
<td>-15.44</td>
<td>6.88</td>
<td>92</td>
</tr>
<tr>
<td>II4a</td>
<td>30.5</td>
<td>3.89 x10⁻³</td>
<td>3.23</td>
<td>51.40</td>
<td>-13.52</td>
<td>7.26</td>
<td>94</td>
</tr>
<tr>
<td>II4b</td>
<td>28.0</td>
<td>2.34 x10⁻³</td>
<td>2.72</td>
<td>61.04</td>
<td>-14.76</td>
<td>6.88</td>
<td>95</td>
</tr>
<tr>
<td>II4c</td>
<td>36.0</td>
<td>1.18 x10⁻²</td>
<td>2.38</td>
<td>69.76</td>
<td>-16.42</td>
<td>6.54</td>
<td>98</td>
</tr>
<tr>
<td>III2a</td>
<td>33.2</td>
<td>7.94 x10⁻⁴</td>
<td>2.12</td>
<td>78.13</td>
<td>-19.63</td>
<td>6.12</td>
<td>82</td>
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<tr>
<td>III2b</td>
<td>34.0</td>
<td>3.16 x10⁻⁴</td>
<td>2.12</td>
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<td>-19.63</td>
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<tr>
<td>III2c</td>
<td>37.5</td>
<td>1.9 x10⁻⁴</td>
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<td>92</td>
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<tr>
<td>III4a</td>
<td>36.5</td>
<td>1.26 x10⁻⁴</td>
<td>2.04</td>
<td>81.38</td>
<td>-18.79</td>
<td>5.88</td>
<td>94</td>
</tr>
<tr>
<td>III4b</td>
<td>36.5</td>
<td>7.59 x10⁻⁵</td>
<td>1.96</td>
<td>84.93</td>
<td>-21.99</td>
<td>5.45</td>
<td>98</td>
</tr>
<tr>
<td>III4c</td>
<td>35.0</td>
<td>5.01 x10⁻⁵</td>
<td>1.85</td>
<td>89.60</td>
<td>-23.11</td>
<td>5.08</td>
<td>98</td>
</tr>
<tr>
<td>Octylphenolb 9-10 EO condensate</td>
<td>31.0</td>
<td>25.00 x10⁻⁴</td>
<td>2.60</td>
<td>62.80</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

*a*HLB Calculated by the formula: $HLB = 20(\text{hydrophilic mol wt} / \text{hydrophobic and hydrophilic mol wt})$

Octylphenolb 9-10 EO condensate (Laurent et al., 2011)

The effectiveness of surface tension reduction ($\gamma_{cmc}$) of the investigated compounds is in agreement with those characterizing the proper quantitative behavior of good surfactants[26]. The surface area demand per molecule A for compounds (II2a-III4c) gradually increases with the alkyl chain length with simultaneous decrease of the $\Gamma max$ values. A `min `values of head group in the surfactants of nonionic series are in range of 48-89 A².

HLB value in Table 2 shows that, a decrease of the molecular weight of the fatty acid results in an increase in the hydrophilic nature of the ester (the HLB value increases). On the other hand, an increase in the number of fatty acid moieties that react with the glycerol ester of dicarboxylic acids will result in a more lipophilic product. However, a narrow distribution of the molecular weight of the prepared nonionic surfactants (II2a-III4c) gave well-defined HLB values (5.45 - 7.68).

To show more clearly the influence of acyl chain length and the number of methylene group of dibasic acid on emulsion properties, the diluted emulsions were observed by optical microscopy (Fig.3) shows clearly that the droplets get smaller with increasing acyl chain length and the number of methylene group of dibasic acid. It is important to note that the emulsions with smaller droplets in the photos are more stable than with bigger droplets [27].

(Fig 4, 5) show the W/O emulsion stability (emulsion preservation ratio) as a function of time for glycerol-based nonionic surfactants (II2a-III4c). The stabilities shown in Table 2 are the preservation ratio at 4hr (Fig.4,5). The effect of the structure composition of glycerol-based nonionic surfactants on the emulsion stability was investigated. The highest stability was obtained for surfactants with two fatty acyl groups (II2a-4c). The stability dropped with a decrease in the number of acyl group, exhibited the poorest stability for surfactants (II2a-4c).
Fig. 4 Stability W/O emulsions as a function of time for surfactants II2a- II4c at room temperature (25 °C).

Fig. 5 Stability W/O emulsions as a function of time for surfactants III2a- III4c at room temperature (25 °C).

The data show that, the glycerol-based nonionic surfactants are effective in keeping the water in the oil phase. A similar results was reported for di acyl glycerol [28].

CONCLUSION

In the present study, new glycerol-based nonionic surfactants have been synthesized and their properties also evaluated. It has been determined that the new glycerol-based nonionic surfactants exhibit in general a good surface-activity and appear then as valuable non-ionic surfactants compared to the most widely used non-ionic surfactants like octyl phenol 9-10 ethylene oxide condensate. The main effect of their attribute molecular structure on the surface-active properties concerns the hydrophobic chain length and follows the same rules as those of classical surfactants. However, they are more surface-active than the corresponding alkyl ester analogues for both cmc and $\gamma_{cmc}$ values.
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REFERENCES