Ethoxylated glycerol monooleate: palm oil based nonionic surfactant for oil-in-water emulsion systems

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Abstract
The present study focuses on the application of ethoxylated glycerol monooleate as a palm oil based nonionic surfactant for oil-in-water emulsion systems. Preparation of the nonionic surfactant was performed in the presence of an alkaline catalyst by reacting glycerol monooleate with ethylene oxide at 80 ºC followed by purification using acetic acid and black carbon. Results show that the stability of emulsion formed by addition of white oil to an aqueous ethoxylated glycerol monooleate was highly affected by the physical and chemical properties of the ethoxylated material. Formulated emulsions using the nonionic surfactant did not demonstrate separation of oil and water phase after centrifugation at 3000 rpm for 10 minutes and therefore potentially used as bio-additive materials in natural cosmetics.

Keywords: nonionic surfactant, ethoxylated glycerol monooleate, palm oil, oil-in-water emulsion

I. INTRODUCTION
There are many types of chemical reactions used in the manufacture of surfactants, such as sulfonation, esterification, ethoxylation, amidation, etc. Ethoxylation in particular is applied to obtain a surfactant which have higher solubility in water properties or have a stronger hydrophilic tail [1]. The level of solubility depends on the amount of ethylene oxide (EO) polymerized and inserted in the structure. Ethoxylated materials as one of the nonionic surfactants are produced in industry by reacting EO with an organic molecule containing mobile hydrogen such as fatty alcohols, alkyl phenols, or fatty acids.

Ethoxylation of fatty esters of rapeseed oil has been reported to be carried out over a homogenous calcium based catalyst [2]. The reaction temperature was found to have subtant influence on the obtained product distribution. With the enhancing development of oleochemistry, palm oil and other readily renewable materials are dominating the market with its oleochemicals. We have previously performed the direct ethoxylation of glyceril fatty esters of palm oil which in dominant were glycerol mono oleate (GMO), at 80-180ºC in the presence of an alkaline catalyst. A degree of polymerization of n = 2, 3 was yielded in the ethoxylated GMO material (EGMO).

Oil-in-water (o/w) emulsion systems stabilized by nonionic surfactants are widely used in agrochemical, cosmetic, food, and pharmaceutical industries [3]. The stability of these emulsion systems, however, still remains a challenging issue to be investigated. Emulsion instability may result from physical processes, i.e. flocculation, coalescence, Ostwald ripening, and gravitation separation. The rate of these changes can be measured by determining the size and distribution of oil droplet in emulsion. Stokes’s law state that the velocity at which a droplet moves is proportional to the square of its radius. The stability of an emulsion to the gravitation separation therefore can be enhanced by reducing the size of droplets [4].

The primary objective of this research is to investigate the critical micelle concentration (CMC) of various EGMO materials with different chemical and physical properties as a nonionic surfactant in an o/w emulsion system and analyze the emulsions formed using centrifugation procedures and optical microscope analysis.

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II. EXPERIMENTAL

A. Materials
Methanol, chloroform, and white oil were purchased from Sigma Aldrich and used in the emulsification process. EGMO was synthesized as previously reported. An amount of GMO and 1% KOH were introduced into a reactor and for 2 hours without heating. EO was then inserted and the mixture was heated at 80ºC for another 2 hours. At the end of the process, the reaction was stirred for 3 hours in room temperature. Purification of EGMO was performed using acetic acid and adsorption with black carbon.

B. Method

1) Preparation of o/w emulsion
An amount of 1 g of selected EGMO was diluted into 100 ml of demineralized water. After stirring, the mixture gradually turned into white and opaque appearance and 0.5 g of white oil was introduced into 10 ml of the mixture and stirred at 2500 rpm in room temperature for 15-30 minutes. The o/w emulsion system formed was then kept in room temperature for stability observation.

2) Surface tension and critical micelle concentration (CMC)
The CMC values of the surfactants were obtained by measurements of surface tension as a function of surfactant concentration at 25ºC on a Sigma 70 tensiometer (Torsion Balance Supplies) equipped with a Pt–Ir du Noüy ring. Measurements were performed in demineralized water. The surface tension values were taken at the breakpoint of the surface tension vs log concentration curve.

3) Stability of o/w emulsion
Stability of the o/w emulsion was tested using centrifuge type Kokosan H-103N series at 3000 rpm for 10 minutes. The emulsion stability was indicated by homogenous phase without separation of the oil and water phase.

4) Optical microscope measurement
The emulsion formed was observed with an optical microscope (Zeiss with Meteor Matrox II software). Magnification was 400x and each emulsion was measured in a 24 hours and 14 days period. Droplet size was recorded and the stability of emulsion was analyzed.

III. RESULT AND DISCUSSION

A. Solubility test of various EGMO in water
EGMO materials were obtained as reported in previous work [5, 6]. Four products was selected for solubility and labeled as A, B, C, and D. Products A, B, and C were all produced in the synthesis at temperatures of 80ºC with different reagent molar ratios whereas D was obtained at a higher temperature at 180º C. The EGMO products were dissolved in 100 ml of water with two concentration types of 0.5% (w/v) labeled as A1, B1, C1 and 1% (w/v) labeled as A2, B2, C2. Product D was used at a single concentration of 1% (w/v). The appearance of various aqueous EGMO at 27ºC is shown in Table 1.

<table>
<thead>
<tr>
<th>Entry</th>
<th>EGMO Product</th>
<th>Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A1</td>
<td>□</td>
</tr>
<tr>
<td>2</td>
<td>B1</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>C1</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>D</td>
<td>■</td>
</tr>
<tr>
<td>5</td>
<td>A2</td>
<td>■</td>
</tr>
<tr>
<td>6</td>
<td>B2</td>
<td>■</td>
</tr>
<tr>
<td>7</td>
<td>C2</td>
<td>■</td>
</tr>
</tbody>
</table>

□ = clear, dissolve, homogeneous (transparent)  ■ = cloudy, homogenous (white, opaque)

A clear dissolved mixture was produced in almost all aqueous EGMO of 0.5% (w/v) (entries 1-3) except for product D (entry 4), meanwhile mixtures became opaque at a higher concentration of 1% (w/v) (entry 5-6). The differences of these appearances are speculated to be caused by the different properties of EGMO product, such as acid value (AV), ester value (EV), molecular weight (MW), hydrophilic-lipophilic balance value (HLB), density, and viscosity as summarized in Table 2.
Table 2. Properties of EGMO selected for emulsification

<table>
<thead>
<tr>
<th>EGMO Product</th>
<th>GMO:EO (mol)</th>
<th>AV (mg KOH/g)</th>
<th>EV (mg KOH/g)</th>
<th>MW (g/mol)</th>
<th>HLB</th>
<th>( \rho ) (g/cm(^3))</th>
<th>( \eta ) (Cp)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1:2</td>
<td>6.07</td>
<td>101.27</td>
<td>460</td>
<td>1.98</td>
<td>0.9855</td>
<td>112.81</td>
</tr>
<tr>
<td>B</td>
<td>1:6</td>
<td>4.29</td>
<td>82.17</td>
<td>878</td>
<td>10.02</td>
<td>1.0244</td>
<td>135.07</td>
</tr>
<tr>
<td>C</td>
<td>1:10</td>
<td>4.14</td>
<td>68.26</td>
<td>1198</td>
<td>12.49</td>
<td>1.0368</td>
<td>67.04</td>
</tr>
<tr>
<td>D</td>
<td>1:1</td>
<td>12.35</td>
<td>105.95</td>
<td>-</td>
<td>-</td>
<td>0.9684</td>
<td>253.64</td>
</tr>
</tbody>
</table>

B. Measurement of CMC value for various EGMO products

The CMC value of EGMO in the current work was determined by a tensiometer and a surface tension vs concentration graph as shown in Fig. 1 was obtained for calculation. From the collected data, it can be seen that the surface tension decreases with the addition of surfactant concentration. The CMC was determined by an interpolation line of surface tension and log concentration of surfactant. The value of CMC is shown in Table 3.

Table 3. CMC value of EGMO

<table>
<thead>
<tr>
<th>Entry</th>
<th>EGMO product</th>
<th>Log CMC (%wt/v)</th>
<th>CMC (%wt/v)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A</td>
<td>-1.9</td>
<td>12</td>
</tr>
<tr>
<td>2</td>
<td>B</td>
<td>-1.2</td>
<td>56</td>
</tr>
<tr>
<td>3</td>
<td>C</td>
<td>-1.3</td>
<td>50</td>
</tr>
<tr>
<td>4</td>
<td>D</td>
<td>-1.8</td>
<td>16</td>
</tr>
</tbody>
</table>

Fig. 1. Surface tension vs concentration graph of EGMO products
C. Optical analysis of o/w emulsion formed using various EGMO products

Emulsions were prepared by adding 0.5 g white oil into 10 ml of aqueous ethoxylatation product. The mixture was stirred for 15-30 minutes at 2500 rpm. The mixture slowly turned into a white opaque solution due to the formation of an emulsion. The stability of these o/w emulsion systems were then tested by centrifugation procedures and optical microscope analysis. Centrifugation was performed at 3000 rpm for 10 minutes, directly after the emulsions were prepared. From the results obtained, it is evident that almost all emulsions did not demonstrate any separation of oil and water phase, except for B1 and C1 which became a two layer mixture after the centrifugation procedure. This indicated that the o/w emulsions formed using various EGMO products generally gave a good stability where the mixture remained homogeneous, white and opaque.

The o/w emulsion was further kept at room temperature and analyzed by optical microscope analysis at two different periods of time. The first analysis was performed after 24 hours (1 day) of storage, and the second was after 14 days (2 weeks). In the case of emulsion kept for 24 hours, it was observed that emulsion A1 and B2 was unstable and two layers were formed. Moreover, no droplets were observed in the solution when analyzed using an optical microscope. This result indicated that emulsion A1 and B2 were only stable for a few hours after the preparation. On the other hand, droplets with various sizes were seen for emulsion A2, C2, and D as illustrated in Fig. 2 and Fig. 3.

Although the droplets observed were not all homogenous with the same size, it can be seen that a double emulsion was formed for emulsion A2. After kept in room temperature for 14 days, however, this was no longer observed due to coalescence. The stability of an emulsion depends gracefully on the size of droplets distributed in the emulsification system. The increase of droplet size results in an unstable emulsion due to coalescence of the droplets in a period of time. Emulsion with different droplet size was also seen for emulsion C2. Smaller droplets are seen in 24 h compared to the 14 days period indicating a higher stability in shorter period of time. In the case of emulsion D however, relatively homogeneous droplets were formed in the first 24 h and no significant change in their size was seen after keeping for 14 days demonstrating a higher emulsion stability compared to other o/w emulsion systems.

![Fig 2. Optical microscope analysis of: (i) A2 – 24 hours, (ii) A2 – 14 days, (iii) C2 – 24 h, (iv) C2 – 14 days](image-url)
IV. CONCLUSION

Ethoxylated glycerol mono oleate (EGMO) from palm oil is active as surfactants of oil-in-water emulsion systems. The nonionic surfactant was synthesized by direct ethoxylation of GMO using ethylene oxide at a temperature of 80 °C in the presence of 1% KOH as catalyst. Purification of the EGMO products by addition of acetic acid and black carbon yielded products with greater acid value, ester value, density and viscosity. The surface tension decreased using all of the EGMO products and a white opaque emulsion was formed by addition of 0.5 g of white oil in 10ml aqueous EGMO. Each product gave different emulsion system which depended on their chemical and physical properties. The emulsions did not observe separation of oil and water phase after centrifugation at 3000 rpm for 10 minutes and therefore are potentially used in the formulation of natural cosmetics.

REFERENCES


