Properties of Palm-Oil-in-Water Emulsions: Effect of Mixed Emulsifiers

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ABSTRACT: Palm-oil-in-water emulsions were prepared with mixtures of Tween 40 and Span 40 in various proportions. Stability and droplet-size distribution of the emulsions were monitored. Interfacial tensions of the palm oil/water interface were determined in the presence of these emulsifier mixtures. Stabilizing efficiency of the emulsifier mixtures was assessed. Synergistic effect of Tween 40 (sorbitan monopalmitate with ~22 moles of ethylene oxide) and Span 40 (sorbitan monooleate) was found on interfacial tension. Tween 40 alone (hydrophilic-lipophilic balance value 15.6) at 1.0% w/w gave palm oil emulsions that were stable for more than 30 days at 2°C. Emulsifier mixtures of Tween 40 and Span 40 with hydrophilic-lipophilic balance values in the range of 8.0–8.6 produced stable emulsions only at much higher emulsifier-mixture concentrations. The inherent nature of the oil and the accompanying natural surface-active materials present in the oil can influence the prevailing conditions at the oil/water interface and alter the composition of the interfacial film and hence its stability.

KEY WORDS: Emulsion stability, interfacial tension, mixed emulsifiers, palm oil emulsion, Span 40, Tween 40.

One of the important components for making an emulsion is the emulsifier, and a systematic selection of emulsifier type for a particular emulsion, is frequently based on the hydrophilic-lipophilic balance (HLB) concept, first introduced by Griffin in 1949 (2). It is used to predict emulsion stability and to control rheological properties. It allows systematic matching of appropriate emulsifiers with oil phases. For example, various researchers have prepared emulsions with mixtures of emulsifiers to achieve the required HLB. Not all results on emulsifier selection and emulsion stability prediction, based on HLB, are consistent, however, as noted previously (3,4). Mickle et al. (5) showed that, for milkfat/water emulsions, the influence of milkfat content on emulsion stability far outweighed that of the emulsifiers’ HLB and type. They attributed this to inaccurate HLB values for the emulsifiers. Tober and Autian (6), using various mixtures of Span and Tween emulsifiers (ICI Specialty Chemicals, Wilmington, DE), were able to determine the optimum HLB value for coconut oil and found that not all emulsions prepared with emulsifier mixtures of the same HLB values had the same stabilities. Conversely, Shinoda and Saito (7) noted that it is difficult to accurately determine the optimum HLB value of an emulsifier from the emulsion stability–HLB relationship. The selection of an emulsifier according to the phase-inversion temperature method may be more accurate and reliable.

It is known that mixtures of emulsifiers can have synergistic effects in enhancing stability of emulsions. Suitable combinations of emulsifiers lead to a greatly enhanced stability as compared to individual emulsifiers (8). Various reasons have been given for this, such as formation of intermolecular complexes at the oil/water (O/W) interface (9) and development of strong interfacial films that prevent coalescence by virtue of its high dilational elasticity (10). Boyd et al. (11) have specifically looked into the influence of HLB of Span–Tween mixtures on stability of paraffin-oil-in-water emulsions. The presence of Span molecules at the interface allows more congeneric geometric packing, resulting in greater cohesion between the lyophobic portions of the Span and Tween molecules. Takamura et al. (12,13) found that O/W emulsions, prepared with Tween 20–Span 80 mixtures, were unstable over the whole HLB range. It was thought (14) that, for emulsifiers with very high or very low HLB, ready desorption of
emulsifiers into the bulk oil or water phase could occur when the oil drops approached each other, resulting in loss of interface stability.

This paper discusses preparation of stable palm-oil-in-water emulsions with mixtures of Span 40 and Tween 40 for possible commercial applications. Both Span 40 (sorbitan monopalmitate) and Tween 40 (sorbitan monopalmitate with 18–22 moles of ethylene oxide) are emulsifiers that are approved for use as food additives. One advantage of using these sorbitan esters and polysorbates is that, in addition to the non-toxicity of the intact esters and their hydrolysides products, changes in the degree of esterification with fatty acids of varying hydrocarbon chainlengths can cover a wide range of HLB values.

MATERIALS AND METHODS

Materials. Double-distilled water from an all-glass apparatus was used. Refined, bleached, and deodorized palm oil (RBDPO), with specifications as shown in Tables 1 and 2, was used for this work. Oil-soluble emulsifier Span 40 and water-soluble emulsifier Tween 40 were supplied by ICI Specialty Chemicals. These were used as received.

Preparation of emulsion. Mixtures of Span 40 and Tween 40, blended to give HLB values as indicated in Table 3, were first prepared. The oil, containing the appropriate concentration of emulsifier mixture, was introduced slowly by pipetting into a fixed volume of water, maintained at 60°C, and stirred by a Ystral homogenizer (Heidelberg Elektro, Kelheim/Donau, Germany) at 8000 rpm for 5 min. This was followed by another 10 min of intensive homogenization at 13,500 rpm after all oil had been added. The following series of emulsions were prepared: (i) two series of emulsions at 23.0% w/w oil with 5.0% w/w and 1.0% w/w, respectively, of emulsifier mixture with HLB between 6.7–15.6; (ii) one series at 50.0% w/w oil but at only 0.1% w/w emulsifier mixture; (iii) one series at 23.0% w/w oil with 0.0025–5.0% w/w Tween 40 only; and (iv) one series with 10.0–80.0% w/w oil with 1.0% w/w Tween 40 only. All samples were stored at 60°C immediately after preparation. The emulsion (50 mL) was placed in a 50-mL measuring cylinder, stoppered, and maintained at 60°C in an oven. Cream height and water layer were measured at regular intervals, while any free oil, if any, could be easily observed as a clear golden-yellowish layer on top of the cream.

Particle size measurement. Emulsion droplet size and size distribution were determined with a Malvern Mastersizer particle size analyzer (laser diffraction technique) (Malvern Instrument, Malvern, Worcester, England). An emulsion was diluted 10 times with warm water before it was transferred into the stirrer chamber of the instrument, which contained 60 mL water at 60°C. Stirrer speed and obscuration were maintained at a constant value of 50% and 0.3, respectively. All particle size measurements were carried out within 10 min after emulsification, unless stated otherwise.

**TABLE 1**

<table>
<thead>
<tr>
<th>Component</th>
<th>% (w/w)</th>
</tr>
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<tbody>
<tr>
<td>Triglycerides</td>
<td>93.4</td>
</tr>
<tr>
<td>Diglycerides</td>
<td>6.6</td>
</tr>
<tr>
<td>Monoglycerides</td>
<td>0.05</td>
</tr>
<tr>
<td>Free fatty acid</td>
<td>0.04</td>
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<tr>
<td>Phospholipid</td>
<td>70 ppm</td>
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**TABLE 2**

<table>
<thead>
<tr>
<th>Fatty acid Composition of Palm Oil Triglycerides</th>
<th>% (w/w)</th>
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<tbody>
<tr>
<td>14:0</td>
<td>1.1</td>
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<tr>
<td>16:0</td>
<td>45.2</td>
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<tr>
<td>18:0</td>
<td>3.7</td>
</tr>
<tr>
<td>18:1</td>
<td>39.9</td>
</tr>
<tr>
<td>18:2</td>
<td>9.7</td>
</tr>
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</table>

**TABLE 3**

<table>
<thead>
<tr>
<th>HLB value</th>
<th>Molar ratio of Span 40/Tween 40</th>
<th>Mean droplet diameter (μm)</th>
<th>Mean droplet diameter (μm)</th>
<th>Mean droplet diameter (μm)</th>
<th>Mean droplet diameter (μm)</th>
<th>Span</th>
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</thead>
<tbody>
<tr>
<td>6.7</td>
<td>10.0</td>
<td>22.38</td>
<td>1.90</td>
<td>11.01</td>
<td>2.22</td>
<td>18.56</td>
</tr>
<tr>
<td>7.59</td>
<td>9.1</td>
<td>8.33</td>
<td>1.48</td>
<td>10.95</td>
<td>1.30</td>
<td>20.83</td>
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<tr>
<td>8.48</td>
<td>8.2</td>
<td>7.44</td>
<td>1.58</td>
<td>10.86</td>
<td>1.31</td>
<td>31.70</td>
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<tr>
<td>9.37</td>
<td>7.3</td>
<td>8.79</td>
<td>1.38</td>
<td>9.84</td>
<td>1.33</td>
<td>25.28</td>
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<tr>
<td>10.26</td>
<td>6.4</td>
<td>8.93</td>
<td>1.40</td>
<td>11.37</td>
<td>1.33</td>
<td>22.48</td>
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<tr>
<td>11.15</td>
<td>5.5</td>
<td>8.64</td>
<td>1.40</td>
<td>10.13</td>
<td>1.35</td>
<td>24.01</td>
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<tr>
<td>12.04</td>
<td>4.6</td>
<td>8.75</td>
<td>1.44</td>
<td>12.25</td>
<td>1.45</td>
<td>24.04</td>
</tr>
<tr>
<td>12.93</td>
<td>3.7</td>
<td>8.65</td>
<td>1.40</td>
<td>10.30</td>
<td>1.36</td>
<td>17.35</td>
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<tr>
<td>14.71</td>
<td>1.9</td>
<td>8.58</td>
<td>1.38</td>
<td>11.26</td>
<td>1.33</td>
<td>25.14</td>
</tr>
<tr>
<td>15.6</td>
<td>0.10</td>
<td>8.89</td>
<td>1.38</td>
<td>9.77</td>
<td>1.40</td>
<td>13.37</td>
</tr>
</tbody>
</table>

*Palm oil concentration (% w/w) = 23*  
*Emulsifier mixture (%)*  
*Span defined as (DIW, 0.9) - (DIW, 0.1)/(DIW, 0.5) is a measure of the polydispersity of the oil droplet in the emulsion. Span 40 and Tween 40 from ICI Specialty Chemicals (Wilmington, DE).  
*Concentration based on oil used.*

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Interfacial tension measurement. A Kruss Site 04 model spinning drop tensiometer (Kruss GmbH, Hamburg, Germany) was used for low interfacial tension measurements at 50°C. The oil (2 μL), containing the emulsifier, was injected into the capillary tube that contained water. Determinations were made with the oil droplets elongated at least four times their radius. Interfacial tension was calculated with a magnification factor of 2.87 and an oil density of 0.8834 g/mL. Higher interfacial tension values were determined with a Kruss K10 tensiometer by the ring method.

RESULTS AND DISCUSSION

One intrinsic characteristic of RBDPO is that its high-melting fraction (stearin) crystallizes on standing at room temperature. Crystallization can be prevented, and the oil remains fluid, if it is kept at 60°C. This is the reason for keeping all the palm oil emulsions at 60°C after emulsification. Formation of crystallites and their subsequent adsorption at the O/W interface would certainly affect the stability of an emulsion (15), and this would complicate interpretation of the role of the emulsifiers.

Emulsion stability. Generally, stable palm-oil-in-water emulsions were opaque and creamy white in appearance. These emulsions were pourable without adhesion to the glass surface of the container. They can be diluted with water, confirming its oil-in-water nature. They creamed readily, but they were easily redispersed by shaking, indicating only weak flocculation of droplets. For unstable emulsions, breaking droplets to form a layer of free oil was obvious. For the purpose of this work, the criterion of stability is only the breaking of emulsion droplets, resulting in phase separation of oil. Such emulsions are considered unstable; creaming is not. For practical reasons, the emulsions studied were observed for a limited period only, because their stability under a vigorous condition of 60°C is itself a good indication of the stability of the emulsion droplets.

At 5.0% w/w emulsifier mixtures in oil, emulsions (at 23% w/w oil) that were stable up to 10 d were formed when HLB values were above 9.37 (see Fig. 1). For HLB values below 8, significant oil separation was noted within 10 d of storage. At HLB 6.7, an oil layer was observed immediately after preparation. Cream height of all emulsions, prepared with emulsifier mixtures with HLB values above 8, was about the same and remained constant after 10 d. It appears that an HLB value of 8 or above is needed to maintain emulsion stability up to 10 d. This seems to point to some critical HLB value that is associated with the most stable emulsion, such as described previously by Becher (16) and Depraetere et al. (17). At 0.1% w/w emulsifier mixtures and 50% w/w oil, emulsification was not achieved because oil separation was noted immediately after stirring stopped, except with Tween 40, which gave relatively stable emulsions, even at 50% w/w oil.

These results were at variance with those of xylene-in-water emulsions in the presence of mixtures of Span 40 and Tween 40, obtained by Tadros (18), who found that the emulsions were not stable in the absence of Span 40. The enhanced stability, both in water and in high electrolyte concentration, was attributed by Tadros (18) to the formation of a more condensed film with a high Gibbs elasticity. The difference in behavior between the present system and theirs can perhaps be traced to the fact that the RBDPO used contained a small amount of natural surface-active materials, such as monoglycerides and phospholipids, which can have a profound influence on interfacial properties of the palm oil/water interface. Both monoglycerides and diglycerides exhibit time-dependent adsorption at the corn oil/water interface (19), and reduction of the steady-state interfacial tension is dependent on composition of the interfacial film. It is envisaged that adsorption of lipids and monoglycerides at the palm oil/water interface would give rise to an interfacial film that consists of more than just Tween 40, and the stability of the emulsion would be altered, regardless of whether Span 40 is present.

Particle size distribution. Table 3 and Figures 2–4 show the particle size distributions of emulsions obtained with 5.0, 1.0, and 0.1% w/w emulsifier mixtures in oil at 23 and 50% w/w oil, respectively. The average particle size increased with a decrease in emulsifier-mixture concentration, and the range of droplet size was the largest for the lowest emulsifier-mixture concentration used. In fact, the unstable emulsions, made from 0.1% w/w emulsifier mixtures, contained droplets as large as 65 μm. This can be explained by insufficient emulsifier coverage of the oildrops at the low emulsifier concentration used (0.1% w/w). It also appears that emulsifier mixtures with low HLB values produced large droplets with a wide range of sizes at all emulsifier-mixture concentrations, which
results in unstable emulsions. Increasing the proportion of Tween 40 in the emulsifier mixture (i.e., increasing HLB value of the mixture) has the effect of narrowing the distribution of droplet size. In the extreme case where only Tween 40 was used (HLB 15.6), an emulsion with the narrowest size distribution was obtained. Mean droplet size of the emulsions was, however, not sensitive to changes in the HLB values in the intermediate range.

Mean droplet size of the emulsions increased no more than 16% with time up to 21 d, beyond which no further change in droplet size was observed (Fig. 5). The size distribution of the emulsions, however, became more polydisperse with time. More large droplets were observed in the distribution, that is, the distribution skewed toward larger droplets. In contrast, a rapid increase in droplet size (up to two to three times the original size) with time during the first 10–20 h has been noted by Tadros (18) on xylene oil drops stabilized by Tween 40. When mixtures of Span 40 and Tween 40 were used, no growth by coalescence was observed, and droplet size remained essentially constant on aging.

Emulsion droplet size is sensitive to Tween 40 concentration, as illustrated in Figure 6 for emulsions (23% w/w oil) C.9. were prepared at constant oil concentration. As emulsifier concentration was increased, mean droplet size decreased, and droplets became less polydisperse. This is similar to behavior already noted for emulsions that were prepared with the emulsifier mixtures. Results indicated that the distribution of droplet sizes was much narrower in the Tween 40 system than in those with emulsifier mixtures. The effect of the Tween 40 concentration on mean droplet size is shown in Figure 7. Below 0.3% w/w Tween 40, droplet size decreased linearly with the log concentration of the emulsifier, whereas droplet size was independent of emulsifier concentration above 0.3% w/w. This behavior was in close resemblance to the interfacial tension vs. log concentration plot of the emulsifier, except that

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Effect of Tween 40 concentration on (a) droplet size of 23% w/w palm oil emulsions and (b) interfacial tension of palm oil/water interface at 50°C. Company source as in Figure 6.

FIG. 8. Effect of oil phase volume on droplet size distribution of 23% w/w palm oil emulsions with 1% w/w Tween 40. Company source as in Figure 6.

FIG. 9. Mean droplet size of 23% w/w palm oil emulsions at various phase volumes with 1% w/w Tween 40. Company source as in Figure 6.
FIG. 10. Effect of concentration of emulsifier (Span 40 and Tween 40) on interfacial tension of palm oil/water interface at 60°C. Company source as in Figure 6.

Facial tension of the O/W interface was reduced to less than 1.0 mN m⁻¹. In comparison, interfacial tension of the palm oil/water interface was 21.1 mN m⁻¹ at 60°C. In contrast, the corresponding palm oil/water interfacial tension of Span 40 was higher and showed a monotonous decrease in interfacial tension at the palm oil/water interface with an increase in emulsifier concentration (Fig. 10). At least 5% w/w Span 40 was needed to bring the O/W interfacial tension to below 1 mN m⁻¹.

In Figure 11, interfacial tension of the emulsifier mixtures against water was plotted at three different emulsifier concentrations. It clearly shows that, at each emulsifier concentration, there was a critical HLB value above which interfacial tension remained constant but below which interfacial tension decreased linearly with HLB values. Critical HLB values were within the narrow range of 8.5–9.5. This observation seems to correlate with the stability data shown in Figure 11, at least for emulsions that contained 5% w/w emulsifier mixture, and it lends some support to the critical HLB stability relationship mentioned previously (16, 17). One should be cautious, however, when interpreting such results because reduction of interfacial tension alone does not necessarily ensure good emulsion stability. For example, Tober and Austin (6) found that, although sucrose monostearate was most effective in reducing interfacial tension of the coconut oil/water interface compared with mixtures of Span 60 and Tween 80, it gave emulsions of poor stability. A similar conclusion was given by Garti and Katz (21) who stressed the importance of adsorption studies of emulsifiers rather than interfacial tension on emulsion stability. For the present system, at 5% w/w emulsifier mixture, interfacial tension was exceedingly low, less than 1 mN m⁻¹.

The close resemblance of interfacial tension plot for emulsifier mixture, compared to that given by Tween 40, suggests a lack of synergistic effect on interfacial tension between Tween 40 and Span 40. It is likely that Span 40 is exerting much influence at the O/W interface because of its good solubility in palm oil. The nature of the oil also has a role to play in the ease with which it can be emulsified (20). Thus, it is not surprising that a completely different finding was obtained by Tadros (18), who showed that a 1:1 mixture of Tween 40 and Span 40 gave the most stable xylene emulsion in water.

Reasonably stable palm-oil–in–water emulsions can be prepared with Tween 40 alone, up to an oil phase volume of 0.5, with no difficulties. Addition of Span 40 to the oil did not appear to confer any synergistic advantage. Instead it was detrimental at low emulsifier–mixture concentrations. The best emulsion was given by Tween 40 (with HLB value of 15) at 1% w/w with a polydispersity of ca. 1.4. Emulsifier mixtures of Tween 40 and Span 40 with HLB value above 15 seemed able to give stable emulsions only at a high emulsifier–mixture concentration of 5% w/w. The unusual stability of the RBPDO emulsion droplets stabilized with Tween 40 at 60°C could well find uses in the manufacture of products, for example, of finely disperse microcrystallites, by spray-drying emulsions of crystallizable oils.

When cooled to room temperature, crystallization of the stearin fraction in the RBPDO emulsion droplets, especially at the droplet surface, resulted in irregularly-shaped particles which, in view of their close proximity in the cream, could lead to their agglomeration in the cream layer. These were easily redispersible. However, if palm olein (with low stearin content) was used instead, droplets of the emulsion (also prepared at 60°C) remained dispersible when stored at room temperature, and there was no change in droplet size on aging (Chow, M.C., unpublished data). Palm oil, being different triglyceride composition from other oils reported in the literature, coupled with the presence of other accompanying natural emulsifiers, is expected to exhibit its own characteristic emulsifying property. Further work is needed to look into
Acknowledgment

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The Variation of Interfacial Tension at the Palm Oil-Water Interface in the Presence of Surface Active Substances

Chow, M C* and Ho, C C*

ABSTRACT

Interfacial tension is a measure of the interactive forces between the oil-water interface. It is important in determining the stability of oil-in-water emulsion.

The interfacial tension of palm oil-water was determined as a function of the concentration of monoglycerides of varying chain length (C12-C18). The interfacial tension decreased with increase in the concentration of monoglycerides and at constant monoglycerides concentration decreased with decrease in chain length. There were also indications that the interfacial tension decreased with the degree of unsaturation of the hydrocarbon chain.

An explanation of the observed lowering of interfacial tension at the oil-water interface was attempted.

INTRODUCTION

Interfacial tension may be described as the interactive force or change in surface free energy at the interface between two immiscible liquids. For a stable system the energy level has to be low. In emulsions a very large interfacial area is involved due to the formation of minute droplets but its interfacial tension may be reduced by the use of surface active substances.

One of the most commonly used surface active agents in the food industry is the monoglycerides and for palm oil to play a more prominent role in the food industry it is vital that some fundamental data regarding the interaction of monoglycerides at the palm oil-water interface be studied.

MATERIALS AND METHOD

99% pure monoglycerides were purchased from Sigma Chemical Co. and used as such. They were 1-monolauryl-rac-glycerol (C12), 1-monomyristoyl-rac-glycerol (C14), 1-monopalmitoyl-rac-glycerol (C16), 1-monostearoyl-rac-glycerol (C18:0), 1-monoooleoyl-rac-glycerol (C18:1, (cis)-9), 1-monolinoleoyl-rac-glycerol (C18:2), (cis)-9,12 and 1-monolinolenoyl-rac-glycerol (C18:3, (cis)-9,12,15) or referred as monolaurin, monomyristin, monopalmitin, monostearin, monoolein, monolinolein and monolinolenin respectively in this paper.

Commercially degummed, neutralized and bleached palm oil (RBD palm oil) was used. Water used was double-distilled.

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Interfacial tension measurements were carried out by the ring method using the Kruss Digital-tensiometer K10 at 60°C.

All the distilled water and additives to the refined oil were prepared a day before the experiment. Before every experiment, the oil and water separately were conditioned in a 60°C oven for at least two hours. The oil/water system was stabilized for another 30 minutes in the measuring chamber.

RESULTS AND DISCUSSION

The interfacial tension at the RBD palm oil-water interface was determined to be 20 mN/m. When monoglycerides ranging from 625–10000 ppm (wt:wt) were added to the oil the interfacial tension was gradually reduced (Figure 1).

Depending on the type of monoglycerides used and at the concentration studied there was a reduction of interfacial tension from 20–6.5 mN/m. For the saturated monoglycerides of chain length C12–C18 at lower concentration the interfacial reduction of each of the different monoglycerides was not distinctly different. At higher 1% concentration the interfacial tension is correspondingly decreased as the chain length is reduced. At 1% concentration of monopalmitin and monomyristin the interfacial tension is very similar. This is possibly due to the inherent monopalmitin which is known to be present in palm oil. The RBD palm oil used in this study contained 0.3% monoglycerides.

The interfacial tension between palm oil and water is affected by the degree of unsaturation of the monoglycerides used (Figure 2). A significant reduction in interfacial tension is observed when the unsaturation is increased by two double bonds as in monolinolein but further decrease is not observed by increasing an additional double bond as in monolinolenin.

![Figure 1. Interfacial tension of refined oil with various concentrations of monoglycerides](image)
CONCLUSION

The interfacial tension between refined palm oil and water is influenced by the chain length of the monoglycerides used. Desaturation of the fatty acid moiety of the monostearin (C18) has a strong influence on the interfacial tension of RBD palm oil-water system. Such data obtained may be of scientific and industrial interest in the processing and extraction of palm oil where a great quantity of water is mixed with palm oil.

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