The Association Structures and Sustainability of Methyl Red and Methylene Blue In Water Systems, A Nonionic Surfactants (Tween-40 And Tween-80) And Cyclohexane

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Abstract - Surfactants mixed with water and oil will form associative structures such as microemulsions and liquid crystals. Microemulsion and liquid crystals can dissolve dyes. Dyestuff solubility is widely used in various industrial fields, for example in paints, textiles, cosmetics and inks. This study aimed to determine the association structure and the solubility of methyl red and methylene blue in the water system, the nonionic surfactant (Tween-40 and Tween-80) and cyclohexane. In this study, 2 association structures have been formed in the water system / Tween-40 / cyclohexane and 3 association structures in the water system / Tween-80 / cyclohexane. Determination of the association structure is done through visual observation and using parafilm at various points in the phase diagram. Methyl red dyes are dissolved in microemulsions and liquid crystals in acidic pH while methylene blue is in alkaline pH so that a stable color is obtained. The average solubility of methyl red in microemulsion is 0.0032 g in 1 gram of the sample and the average solubility of methyl red in the liquid crystals is 0.0033 grams in 1 gram of sample. As for the average solubility of methylene blue in the microemulsion is 0.0013 grams in 1 gram of the sample and the average solubility of methylene blue in the liquid crystal by 0.0014 g in 1 gram of sample. The measurement of the refractive index in some samples showed methyl red and methylene blue dissolved homogeneously in the sample. The refractive index value of the sample after dissolving the dye is higher than the refractive index value before the dyestuff is dissolved, because the dye changes the composition of the sample. The viscosity of the microemulsion before the dyestuff is dissolved is lower than the viscosity that has been dissolved by the dyestuff.

Keywords — Association Structure, Solubility, Dyestuff, Bias Index, Viscosity.

I. INTRODUCTION

Surfactant is an effective surface active agent to reduce the surface tension of the medium which has a hydrophilic group (like water) in the head and hydrophobic groups (like oil) on the tail [1]. Surfactants can form associative structures when mixed in water and oil. The association structure is micelles, liquid crystals and microemulsions [2].

Microemulsion has features, including; transparent, thermodynamically stable, low surface tension, has a small refractive index, dissolves hydrophobic compounds into a hydrophilic system, is spontaneous, easy to manufacture, high solubility capacity, low viscosity, and can dissolve dyes [3]. In addition to microemulsions, the lamellar liquid crystal area can also dissolve dyes [4].

The testing of dye solubility carried out in the microemulsion and liquid crystal regions is an interesting study because it is widely used in various industrial fields, for example in paints, textiles, cosmetics and inks. Dyestuffs that are usually widely used in the industrial world are methyl red and methylene blue [5]. Methyl red and methylene blue are non-polar organic dyes which have very little solubility in water [6].

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Previously, research had been done on the association structure and solubility of methyl yellow and carbon black in water systems, cyclohexane and surfactants (Tween-40 and Tween-80) in water pH = 1 and pH = 5. In Tween-40 two phase regions were obtained, namely microemulsion and lamellar liquid crystals whereas in Tween-80, three phase regions were obtained, namely microemulsion, lamellar liquid crystals and hexagonal liquid crystals [7].

Solubility test of methyl yellow and carbon black was carried out on microemulsion because the structure was not rigid compared to lamellar and hexagonal liquid crystals. This dye solubility can be used as ballpoint ink and printer cartridge.

Ink ballpoint and printer cartridges generally consist of four colors, namely red, yellow, blue and black. For the availability of yellow and black, research has been conducted, while for permanent blue color can be produced from methylene blue and permanent red color can also be produced from methyl red. Therefore, the researchers are interested in continuing this research with the title “the association structure and solubility of methyl red and methylene blue in the water system, nonionic surfactants (Tween-40 and Tween-80) and cyclohexane.”

II. METHODOLOGY

The research was conducted at the Chemical Research Laboratory of the Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Negeri Padang.

2.1 Tools and Materials

The tools used are glassware, drop pipettes, test tubes (PYREX code TSR SCR-13-100), vortex mixers (thermo scientific model no. M37610-33), analytical balance (Acculab Sartorius Group d = 0.0001), pH meter, refractometer (ABEE 2WAJ), centrifuge (system laboratory instrument), magnetic station, Ostwald viscometer, 1 mL piknometer (PYREX) and parafilm.

The materials used in this study were aquabidestilata, cyclohexane (Merck, 99.5%), Tween-40 (Merck), Tween-80 (Merck), methyl red (Merck), methylene blue (Merck), nitric acid (Merck, 69%) and KOH.

2.2 Water preparation pH = 4.5, pH = 7 and pH = 9.5

The concentrated nitric acid solution is dripped little by little into 250 mL of aquabidestilata in a beaker. Stirred with magnetic stirrer and observed pH changes with pH meter. Nitric acid is added to the desired pH (pH = 4.5).

Potassium hydroxide solution is dripped little by little into 250 mL of aquabidestilata in a beaker. Stirred with magnetic stirrer and observed pH changes with pH meter. Potassium hydroxide added to the desired pH (pH = 7 and pH = 9.5).

2.3 Determination of the composition of water, surfactant, and cyclohexane

Take points at certain coordinates on ternary diagrams. Then, calculate the composition for the percentage of water, surfactant and cyclohexane in mass ratio, so that the total mass of the three components becomes 0.5 grams

2.4 Determination of the association structure of Tween-40 and Tween-80 in the water system (pH = 4.5, pH = 7 and pH = 9.5) and cyclohexane

Tween-40, water pH = 7 and cyclohexane are put into a test tube according to the composition that has been determined and homogenized using a vortex mixer. The surfactant association structure formed was observed visually using parafilm to distinguish between microemulsion and liquid crystal phases. In the liquid crystal area, visual observations were made to distinguish lamellar and hexagonal liquid crystals. Hexagonal liquid crystals if in vortex will be stiff and lamellar liquid crystals if the vortex moves. Determination of the association structure is carried out at various coordinate points (± 200 points) found on ternary diagrams to distinguish microemulsion and liquid crystal regions. The same procedure is performed on water pH = 4.5 and water pH = 9.5 and followed by Tween-80 using the same procedure in Tween-40.

2.5 Test of the solubility of methyl red and methylene blue

Several coordinate points on the microemulsion (W / O) and lamellar liquid crystals in the mapped areas were marked and then the solubility test was carried out. Small amounts of methyl red (in grams) are added little by little to 1 gram of microemulsion (W / O) or 1 gram of lamellar liquid crystals from the water system / Tween-40 / cyclohexane and water / Tween-80 / cyclohexane which has been determined. Additioning is stopped when deposits begin to form. The optimum methyl red mass until the saturation solution occurs is the optimum solubility of methyl red. The same procedure is also carried out to determine the solubility of methylene blue.

2.6 Measurement of refractive index

Drop as much as three drops onto a sample glass on a refractometer. After the sample is dropped, close the
The source of the light is turned on and the tool scale reading is set at the refractive index of 1.30. Through the ocular lens we can see the dark state of light at the top scale that can be adjusted using a knob on the right side. After a bright dark state is obtained. Pay attention to the scale of the numbers below the dark light. Refractive index measurements are carried out at room temperature and then converted to a temperature of 20°C.

\[ n_{\text{sample}} = n_T + (T - 20) \times 0.0005 \]

*n*<sub>sample</sub> : sample refractive index,

*n*<sub>T</sub> : refractive index at room temperature,

T : room temperature when measuring.

### 2.7 Viscosity Measurement

Viscosity measurements are carried out using an Ostwald viscometer which has two lines, first line and second line. As much as 1 mL of microemulsion is inserted past the upper limit mark, after concave below the microemulsion is right on the first line, the stopwatch starts. The time calculation will be stopped when the concave below the microemulsion that flows through the capillary tube touches the second line. The time (t) needed by the microemulsion to pass through the capillary tube will be used as data used in the calculation to determine the viscosity of the microemulsion. The same is done with water as a comparison liquid to measure the viscosity of microemulsions. The equation used in measuring viscosity is based on the following Poiseuille law:

\[
\eta = \frac{\eta_1}{\rho_2 t_2} = \frac{\eta_2}{\rho_1 t_1}
\]

\[ \eta = \text{viscosity of the solution (poise)} \]

\[ \rho = \text{density of liquid (g/cm}^3\text{)} \]

### III. RESULTS AND DISCUSSION

#### 3.1 Phase diagram preparation and determination of association structure

To obtain the surfactant association structure (especially microemulsion and lamellar liquid crystals) phase preparations were prepared. Phase diagrams of the water system, nonionic surfactants (Tween-40 and Tween-80) and cyclohexane are obtained by titrating the mixture of water and cyclohexane with surfactants until turbidity is obtained. In the water system / Tween-40 / cyclohexane obtained 2 association structures, namely microemulsion and lamellar liquid crystals shown in Figures 1, 2 and 3.

![Figure 1. The diagrams of water system phase, Tween-40 and cyclohexane at pH = 4.5](image1.png)

Figure 1. obtained two association structure areas, namely microemulsion and lamellar liquid crystal. The area of microemulsion was obtained in the water region 0% -26%, Tween-40 15% -100%, and cyclohexane 0% -85%. In lamellar liquid crystals obtained in the water region 5% - 44%, Tween-40 16% -84%, and cyclohexane 0% -76%.

![Figure 2. The diagram of water system phase, Tween-40 and cyclohexane at pH = 7](image2.png)

Figure 2. obtained two association structures, namely microemulsion and lamellar liquid crystal in the water system / Tween-40 / cyclohexane at pH = 7. The microemulsion region was obtained in the water area of 0% - 20%, Tween-40 15% -100%, and cyclohexane 0% -85%. In lamellar liquid crystals obtained in the water region 5% - 50%, Tween-40 17% -80%, and cyclohexane 0% -74%.
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Figure 3. The diagrams of water system phase, Tween-40 and cyclohexane at pH = 9.5

Figure 3. obtained three areas of association structure namely microemulsion and lamellar liquid crystals in alkaline pH water which is 9.5. The area of microemulsion was obtained in the water region 0% - 25%, Tween-40 16% - 100%, and cyclohexane 0% - 85%. Whereas for lamellar liquid crystals obtained in the water region 5% - 44%, Tween-40 16% - 81%, and cyclohexane 0% - 75%.

In the Tween-80 / cyclohexane water system, the three associative structures were obtained, namely microemulsion, lamellar liquid crystals and hexagonal liquid crystals shown in Figures 4, 5 and 6.

Figure 4. The diagram of water system phase, Tween-80 and cyclohexane at pH = 4.5

Figure 4. obtained 3 association structure regions, namely microemulsion, lamellar liquid crystal, and hexagonal liquid crystal in acidic pH water which is 4.5. The area of microemulsion was obtained in the water area of 0% - 21%, Tween-80 15% - 100%, and cyclohexane 0% - 85%. In lamellar liquid crystals found in water areas 7% - 39%, Tween-80 26% - 82%, and cyclohexane 0% - 63%. Whereas hexagonal liquid crystals were found in water areas 19% - 50%, Tween-80 26% - 64%, and cyclohexane 1% - 51%.

The association structure that is formed from three-component mixing can be distinguished visually such as microemulsions in the form of clear and transparent liquid, while liquid crystals are slightly cloudy, not transparent and thick. Besides being distinguished visually, microemulsion and liquid crystals can also be distinguished using parafilm.

Figure 5. The diagram of water system phase, Tween-80 and cyclohexane at pH = 7

Figure 5. A water system / Tween-80 / cyclohexane at pH = 7 obtained 3 association structures namely microemulsion, lamellar liquid crystal, and hexagonal liquid crystal. The area microemulsion was found in water areas 0% - 23%, Tween-80 16% - 100%, and cyclohexane 0% - 84%. In lamellar liquid crystals obtained in the water region 6% - 38%, Tween-80 30% - 84%, and cyclohexane 0% - 60%. Whereas for hexagonal liquid crystals obtained in the water area of 20% - 47%, Tween-80 27% - 66%, and cyclohexane 1% - 45%.
If observed using parafilm liquid crystals will glow, while microemulsions do not glow [8].

3.2 Solubility of red dyes and methylene blue

In this study, the dissolved dyestuffs were methyl red and methylene blue in the microemulsion area and lamellar liquid crystals. In conditions of pH = 4.5 tested the solubility of methyl red dyes, pH = 7 in the methyl red dye and methylene blue while pH = 9.5 was seen by the solubility of the methylene blue dye.

Table 1. Comparison of the average solubility of methyl red and methylene blue in microemulsion samples and lamellar liquid crystals

<table>
<thead>
<tr>
<th>Tween</th>
<th>Phase</th>
<th>The average value of the solubility of dye</th>
<th>Methyl red</th>
<th>Methylene blue</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH=4,5</td>
<td>pH =7</td>
<td>pH =7</td>
<td>pH</td>
</tr>
<tr>
<td>40</td>
<td>Microemulsion w/o</td>
<td>0,003</td>
<td>1</td>
<td>0,0012</td>
</tr>
<tr>
<td></td>
<td>Lamellar liquid crystal</td>
<td>0,003</td>
<td>3</td>
<td>0,0014</td>
</tr>
<tr>
<td>80</td>
<td>Microemulsion w/o</td>
<td>0,003</td>
<td>3</td>
<td>0,0012</td>
</tr>
<tr>
<td></td>
<td>Lamellar liquid crystal</td>
<td>0,003</td>
<td>3</td>
<td>0,0014</td>
</tr>
</tbody>
</table>

Dyestuffs are dissolved in the w/o microemulsion region which has less water composition than the cyclohexane composition. Methyl red is a semi-polar dye which can dissolve in polar solvents such as water and non-polar solvents such as cyclohexane while methylene blue is a polar dye that dissolves easily in water, so the solubility of methyl red is higher than the solubility of methylene blue in microemulsions. Likewise with solubility in lamellar liquid crystals, where the composition of water in lamellar liquid crystals is below 50% so that the solubility of methylene blue is lower than the solubility of methyl red.

The solubility of dyes in microemulsions and liquid crystals does not depend on the fractions involved but only on the solvent medium such as aggregate form, microemulsion drop size and liquid crystals. Because the dyes dissolved in the microemulsion are not present on the inside or outside of the microemulsion but follow the form of surfactant associations [9]. Illustration of the solubility of dyes in microemulsions and liquid crystals can be observed in Figure 7 [10].

Figure 7. Illustration of dye solubility of methylene blue in microemulsion and lamellar liquid crystals

Figure 8. A water system / Tween-80 / cyclohexane at pH = 7 obtained 3 association structures namely microemulsion, lamellar liquid crystal, and hexagonal liquid crystal. The area of microemulsion was found in water areas 0% - 23%, Tween-80 16% - 100%, and cyclohexane 0% - 84%. In lamellar liquid crystals obtained in the water region 6% - 38%, Tween-80 30% - 84%, and cyclohexane 0% - 60%. Whereas for hexagonal liquid crystals obtained in the water...
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area of 20% -47%, Tween-80 27% -66%, and cyclohexane 1% -45%.

Figure 8. The diagram of water system phase, Tween-80 and cyclohexane at pH = 7

Figure 9. obtained 3 association structures namely microemulsion, lamellar liquid crystal, and hexagonal liquid crystal. The microemulsion area was obtained in the water area of 0% -28%, Tween-80 15% -100%, and cyclohexane 0% -85%. In lamellar liquid crystals it was found in water areas 7% -39%, Tween-80 26% -82%, and cyclohexane 0% - 63%. Whereas hexagonal liquid crystals were found in water areas 19% -50%, Tween-80 26% -64%, and cyclohexane 1% -51%.

Figure 9. The diagram of water system phase, Tween-80 and cyclohexane at pH = 9.5

The association structure that is formed from three-component mixing can be distinguished visually such as microemulsions in the form of clear and transparent liquid, while liquid crystals are slightly cloudy, not transparent and thick. Besides being distinguished visually, microemulsion and liquid crystals can also be distinguished using parafilm. If observed using parafilm liquid crystals will glow, while microemulsions do not glow [8].

3.3 Refractive Index

Refractive index measurement is done to see the relationship of the sample composition with the refractive index of the sample and the refractive index of the sample after the addition of dyes. From the results of measuring the refractive index can be obtained information on the relationship of the addition of dyes with the samples tested and homogeneity of the sample.

Refractive index measurements were carried out on microemulsion samples and lamellar liquid crystals. Refractive index measurements are carried out at room temperature and then converted into a temperature of 20˚C using a formula.

\[ n_{\text{sample}} = n_T + (T - 20) \times 0.0005 \]

Where \( n_T \) : refractive index at room temperature

\( T \) : room temperature when measuring

The measurement results of the average refractive index on microemulsion samples and lamellar liquid crystals are illustrated in Figures 10 and 11.

Figure 10. Average value of the refractive index on microemulsions
From the measurement results can be seen the value of the refractive index of microemulsions and liquid crystals dissolved by dyes higher than the refractive index values of microemulsions and liquid crystals without dyes, this is due to the presence of microscopic dyes that dissolve. As a result, dyes change the composition of the microemulsion which results in changes in the refractive index. The highest refractive index on microemulsions was in the water system pH = 7 / Tween-80 / cyclohexane in the solubility of methyl red dye and the highest refractive index in the lamellar liquid crystal was in the water system pH = 4.5 / Tween-80 / cyclohexane in the solubility of the substance methyl red color. The index is refractory to colorless microemulsion in water systems pH = 9.5 / Tween-40 / cyclohexane and the lowest refractive index in lamellar liquid crystals without dyes in the water system pH = 9.5 / Tween-80 / cyclohexane.

The water refractive index is 1.333 and 1.424 cyclohexane. w/o microemulsion samples had a high refractive index compared to o/w microemulsion. w/o microemulsion consists of an oil-rich environment while the o/w microemulsion consists of a water-rich environment. So that the w/o microemulsion samples will have a refractive index that is close to the cyclohexane refractive index and higher than the refractive index of o/w microemulsion samples [11].

### 3.4 Viscosity Measurement

Viscosity measurements were only carried out for microemulsion samples and were not carried out on lamellar liquid crystal regions because the lamellar liquid crystal structure was more compact than microemulsion. This viscosity measurement has a purpose to find out how the structure changes based on the function of the composition of the water and the thickness of the microemulsion. Flow velocity is different because of differences in viscosity. The amount of viscosity is expressed by a number that states the thickness of a liquid. The viscosity of each fluid is different and expressed quantitatively by the viscosity coefficient [12]. An increase in viscosity can be observed in Figure 12.

Based on the picture above, it can be seen that the viscosity increases with the addition of water composition with the addition of dyestuff (methyl red and methylene blue) and without the addition of dyes. The highest viscosity in microemulsion with the addition of methyl red dye was 64.27 cP, while the addition of methylene blue dye was 62.98 cP and without the addition of dyestuff was 60.39 cP. The lowest viscosity on microemulsion with the addition of methyl red dye is 29.95 cP, while the addition of methylene blue dye is 21.43 cP and without the addition of dye is 19.21 cP.

Microemulsions have greater viscosity compared to water. This is because the constituent components of the microemulsion (surfactant, water, oil) form an aggregate which causes the structure of the microemulsion to be denser, so that the microemulsion is thicker than water [13].

The viscosity value after adding dyes is greater than before adding dyes. It is assumed that the addition of dyestuffs causes the intermolecular distance of microemulsions to become smaller so that the interaction between microemulsion molecules becomes greater. Large inter-molecular interactions cause greater viscosity. A greater viscosity value after the addition of a dye indicates that the microemulsion becomes thicker after adding dyes [14]. The microemulsion viscosity value has fulfilled the theoretical requirements, where the viscosity value of microemulsion has a value of ≤ 200 cP [15].
IV. Conclusion

Based on the research that has been done, it can be concluded that:

1. Water systems (pH = 4.5; pH = 7 and pH = 9.5), nonionic surfactants (Tween-40 and Tween-80) and cyclohexane produce microemulsion association structures, lamellar liquid crystals and hexagonal liquid crystals.

2. Changes in pH do not significantly affect the resulting phase diagram because the surfactants used are nonionic surfactants.

3. Methyl red solubility is higher than solubility of methylene blue because it is dissolved in w/o microemulsion, where methyl red is semi polar which can dissolve in cyclohexane and water.

4. Addition of dyes to microemulsions and liquid crystals causes an increase in the refractive index value because dyes dissolve microscopically.

5. The viscosity of the microemulsion changes before and after the dye is added due to changes in the microemulsion structure.

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