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Association structure and solubility dynamic of methyl red and methylene blue in the system of water, sodium dodecyl benzene sulfonate and pentanol

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Abstract. The purpose of this study was to determine the association structure, solubility, and homogeneity of methyl red and methylene blue in the system of water, sodium dodecylbenzene sulfonate (SDBS), and pentanol system, and to analyze the morphology of the association structure before and after dissolved in methyl red and methylene blue. The mass ratio composition of water/SDBS/pentanol system at pH 4.5, 7, and 9.5 selected from created Terner phase diagram to obtain the association structures. From the obtained association structures, the solubility of methyl red at pH 4.5 and methylene blue at pH 7 and 9.5 was analyzed. The homogeneity of methyl red and methylene blue was determined by the refractive index. The results showed that two association structures namely microemulsion (water in oil (*w/o*) and oil in water (*o/w*)) and lamellar liquid crystal phase was obtained. The maximum solubility of methyl red was found in *w/o* microemulsion. Meanwhile, the maximum solubility of methylene blue was found in *o/w* microemulsion. Refractive index results showed that mostly methyl red and methylene blue dissolved in the sample homogeneously. The structure of the liquid crystal microemulsion changed after the addition of methyl red and methylene blue observed by the Optical Polarizing Microscope.

1. Introduction

Dyes are organic compounds that are used to give color to an object. The dye molecule is a combination of organic dyes that have unsaturated groups that can undergo a transition called chromophore with several other groups that cannot undergo a transition but can undergo an electron transition called autochromes [1].

Dyes are divided into two, namely organic dyes which are polar, and dyes which are nonpolar. Organic dyes that are polar are organic dyes methyl red and methylene blue. Methyl red is an ionic dye which has a large solubility in acidic pH, while methylene blue is a cationic dye that can dissolve in water which is equally polar [2] [3]. Methyl yellow is a non-polar dye because it dissolves in alcohol, ether, strong acids, and is difficult to dissolve in water [4].

The dye is widely used in industrial fields such as inks, paints, and as a dye for silk or wools. The red color can be obtained from methyl red and the blue color can be obtained from methylene blue. Many industries use methyl red and methylene blue because methyl red is difficult to degrade and high intensity, while methylene blue is widely used for dyes in the silk industry because of the strong adsorption of methylene blue [3] [5].

Research on the solubility of dyes has been carried out previously [6], namely the solubility of organic dyes methyl red and methylene blue in water microemulsion, anionic surfactants (SDBS), and pentanol system. The solubility produced by water in oil microemulsion is still low. Through the sol-gel method with the gelation process, a gel that has a higher solubility than microemulsion was produced [7]. The results obtained were that the solubility of water-in-oil microemulsion gel in water, Brij surfactant, CTAB, and pentanol system was higher than the microemulsion. The preparation was related to the solubility of organic dyes in surfactant microemulsions [8].

The microemulsion is a dispersion system between oil and water whose surface between phases is stabilized by surfactants. Microemulsion can function as a dye solvent medium. Microemulsions have a higher level of solubility and are thermodynamically stable substances when obtained from mixtures in the right proportions so that they can dissolve non-dissolving liquids [9] [10]. With a microemulsion medium, the dye can be dissolved easily even in a water-rich medium [11].

The microemulsion is divided into two, namely water in oil microemulsion and oil in water microemulsion. The microemulsion that is prepared to become a gel is water in oil microemulsion because the water in oil microemulsion has a higher solubility than oil in water microemulsion [12]. The microemulsion is one of the association structures of surfactants. Microemulsion consists of polar water, hydrocarbon oil which is non-polar and is stabilized by surfactants.

Surfactants are surface-active ingredients consisting of the head and tail. The head is hydrophilic and the tail is hydrophobic. Hydrophilic is polar or is called water-like and hydrophobic is non-polar or doesnot like water. Therefore, surfactants can reduce surface tension. Surfactants can function as cleaners because they have an association structure. One of the surfactants that can be used as a cleaning agent is SDBS surfactant [13].

SDBS surfactants can form an association structure, one of which is to form a water in oil microemulsion. Based on this, researchers have completed research on the solubility of organic dyes methyl red and methylene blue in water-in-oil microemulsion gelation, anionic surfactant (SDBS), and pentanol. Gel preparation was based on the water in oil microemulsion mapping area [6]. The mapping results can be seen in figures (1 and 2)

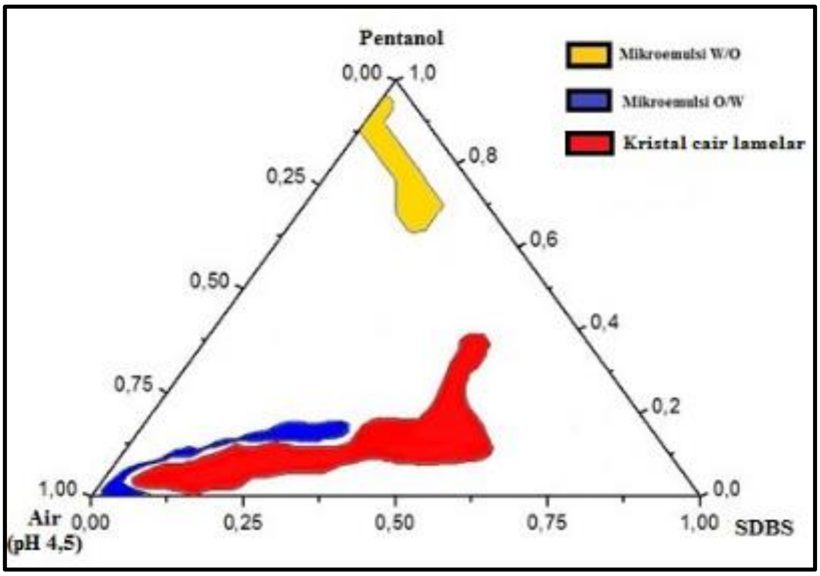

Figure 1. Phase diagram of water/SDBS/pentanol system at pH 4.5[10]

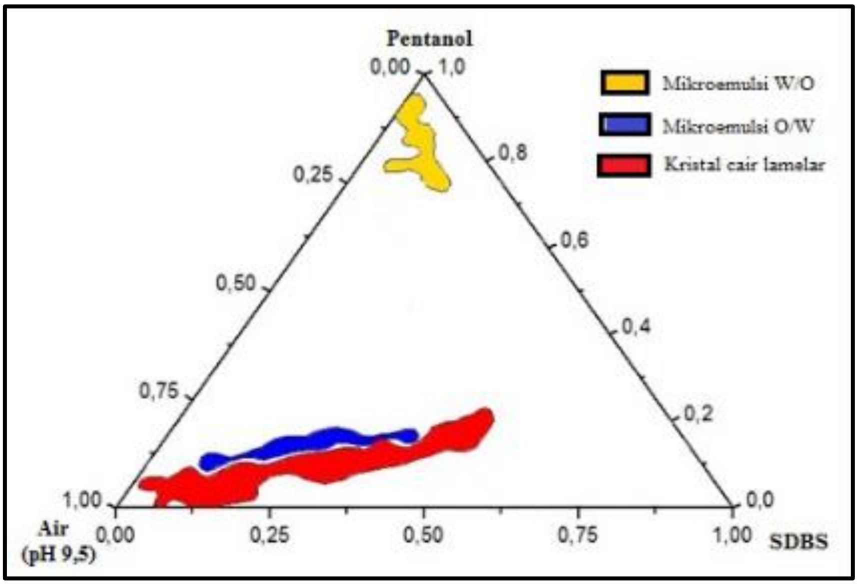

Figure 2. Phase diagram of water/SDBS/pentanol system at pH 9.5[10]

2. Method

2.1. Tools and Materials

The tools used in this study consisted of pH meters, glassware (Erlenmeyer, test tubes, beaker, dropper pipette) (PYREX code TSR SCR-13-100), vortex maxi mix (Thermo scientific model no M37610-33), analytical balance (Acculab, Sartorius Group d = 0.0001), water bath, spatula, magnetic stirrer, and mercury thermometer. The materials used were Sodium Dedocylbenzene Sulfonate (Merck), aquabidestilata, pentanol (Merck, 99.5%), TEOS, ethanol, nitric acid (Merck, 69%), methyl red and methylene blue, and KOH.

2.2. Acid and *alkaline medium preparation*

Take 50 ml of aquabides and put it in a beaker, then add 2 M HNO3 dropwise while stirring. The addition of a drop of 2 M HNO3 solution was carried out until the pH of the solution reached 4.5. Take 50 ml of aquabides and put it in a beaker, then add 2 M KOH dropwise while stirring. The addition of a drop of 2 M KOH solution was carried out until the pH of the solution reached 9.5.

2.3. Gel preparation

Gelation preparation was carried out by adding TEOS and ethanol to water in oil microemulsion with a ratio of water and TEOS 1: 8. Then homogenized using a vortex mix for 15-30 minutes until the sol was formed. After that, it was heated using a water bath at 65^{o}C until it forms a gel. Water in oil microemulsion samples was digested based on the Mahda phase diagram mapping (figures 1 and 2).

2.4. Organic dye solubility test

The solubility test for organic dyes methyl red and methylene blue was carried out by adding each dye sample to the water in oil microemulsion gel. The addition was done by gradually adding the dye until it did not dissolve in the gel anymore. Methyl red was dissolved in water in an oil microemulsion gel water system (pH = 4.5)/SDBS/Pentanol system. Methylene blue was dissolved in microemulsion gel water in an oil-water (pH = 9.5)/SDBS/Pentanol system.

3. Results and discussion

3.1. Gelation Preparation from water in oil microemulsion

Water in oil microemulsion consists of water (pH 4.5 and pH 9.5), surfactant (SDBS), and pentanol system which is a clear and transparent liquid as shown in figure 3.a. When the water in oil microemulsion was added with TEOS and ethanol, it will form a transparent sol at pH 4.5 and pH 9.5 for each SDBS surfactant, as can be seen in Figure 3.b. After being vortexed, heated using a water bath at 65 ^oC, a dense and cloudy gel that is not transparent is formed as shown in Figure 3.c.

Figure 3. Sample of water in oil microemulsion gelation. a. water in oil microemulsion, b. Water in oil microemulsion sol, c. Water in oil microemulsion gel.

The addition of TEOS functions to form a silica matrix in gel formation so that the microemulsion density of water in oil is small [15]. The addition of TEOS based on the TEOS: water mole ratio was 1: 8 which can be seen in table 1 while the addition of ethanol-based on the TEOS: ethanol ratio was 1: 1.

Table 1. The amount of TEOS added to the sample pH 4.5

No	SDBS (gr)	Air (gr)	Pentanol (gr)	TEOS (gr)
2	0,03	0,07	0,9	0,10127
3	0,04	0,07	0,89	0,10127
4	0,06	0,07	0,87	0,10127
5	0,08	0,07	0,85	0,10127
7	0,02	0,1	0,88	0,14467
8	0,05	0,09	0,86	0,13020
10	0,06	0,1	0,84	0,14467
11	0,035	0,095	0,865	0,13743
16	0,06	0,06	0,88	0,08680
19	0,03	0,06	0.91	0,08680
21	0,03	0,05	0,92	0,07233
20	0,03	0,08	0,89	0,11573

Table 2. The amount of TEOS added to the sample pH 9.5

No	SDBS (gr)	Air (gr)	Pentanol (gr)	TEOS (gr)
3	0,04	0,1	0,86	0,13743
7	0,05	0,08	0,87	0,11573
8	0,07	0,07	0,86	0,10127
12	0,03	0,06	0,91	0,08680

If the microemulsion of water in oil is given a bundle of light then the light will continue, because the particles in the microemulsion are far away so that the light given will continue. Similarly, the microemulsion of water in oil in the form of soles is given a bundle of light then the light will be continued because the particles from the sol are not close to each other. While the microemulsion of water in oil in the form of a gel is given a bundle of light then the light will not be continued because the particles in the microemulsion have been close to each other as seen in illustration figure 4.

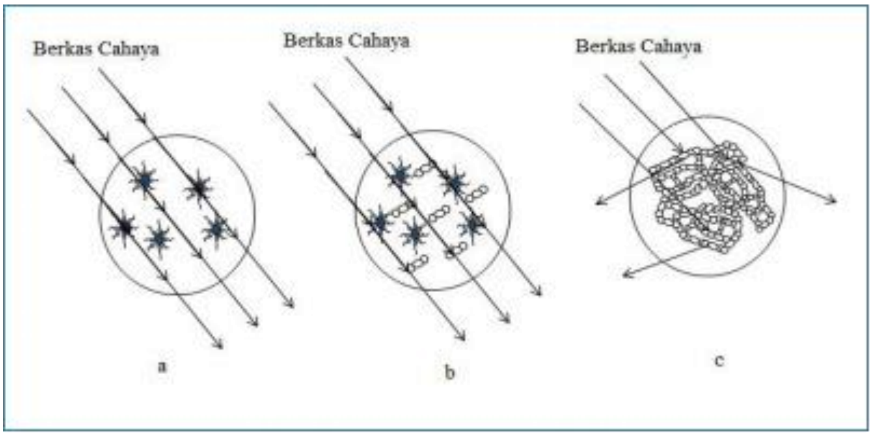

Figure 4. Illustration of the distance between particles (a) microemulsion water in oil, (b) solvent microemulsion water in oil, and (c) gel microemulsion water in oil [7].

3.2. The solubility of organic dyes methyl red and methylene blue
The solubility of methyl red dye in water in oil microemulsion gel has an average solubility amount of 0.00398 grams or 3.98 mg / g in weight percent in 1 gram of sample while the average solubility of methyl red dye in water in oil microemulsions is 0.00167 gram or 1.67 mg / g in percent by weight for 1 gram sample. The solubility of water in oil microemulsion gel before and after adding the dye can be seen in figure 5.

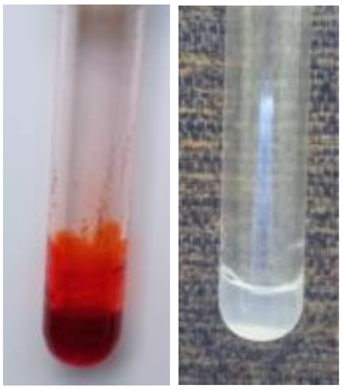

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Figure 5. Sample solubility of methyl red in water in oil microemulsion gel in the composition of water (pH 4.5), SDBS, and pentanol. (a) gel before the methyl red dye was dissolved, (b) gel after the methyl red dye was added.

The solubility of methylene blue dye in water in oil microemulsion gel in the composition of water (pH 9.5), SDBS, and pentanol system can be seen in figure 6. Water in oil microemulsion gel has an average solubility of 0.00375 grams or 3.75 mg / g was higher than the water in oil microemulsion solubility which had an average solubility of 0.001175 grams or 1.17 mg / g in 1 gram of sample.

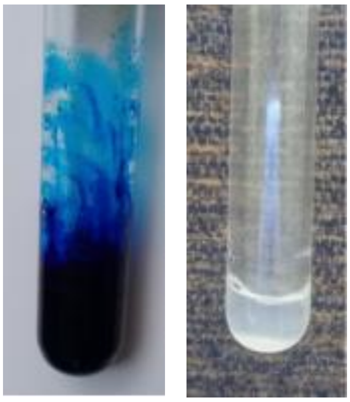

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Figure 6. Sample solubility of methylene blue in water in oil microemulsion gel in the composition of water (pH 9.5), SDBS, and pentanol system. (a) gel before dissolving the methylene blue dye, (b) gel after adding the methylene blue dye.

Methyl red and methylene blue are both polar but methyl red in acidic conditions has a polar group structure at both ends so that methyl red can dissolve in water in oil microemulsions which contain a little water composition in acidic conditions and water in oil microemulsions have solubility which big. Methylene blue has a higher solubility in the oil in water microemulsion because methylene blue has a high solubility in the water while the medium used for dye solubility in water in oil microemulsion which has a water content that is slightly less than oil so that the average solubility value of methyl red higher than the average solubility value of methylene blue in gel and water in oil microemulsion [2].

When compared to the solubility value of the gel solubility with water in oil microemulsion, the solubility value of the Methyl red and methylene blue dyes in the water in oil microemulsion gel was higher than the water in oil microemulsion dye solubility value because the gel contained cavities between particles as shown in figure 7. and during gel preparation, there was the addition of TEOS and ethanol which made the solubility of the dye higher in the gel. The interaction of the dipole moment between the positive dipole moment on the gel particles and the negative dipole moment on the dye particles can also result in higher solubility in the gel in water in oil microemulsions, as in illustration figure 8.

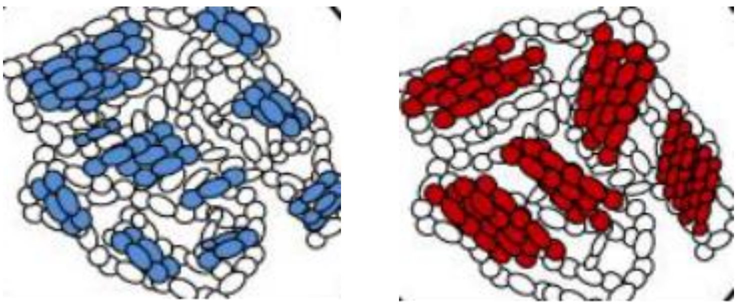

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Figure 7. (a). Methyl red fills the gel cavity, (b) methylene blue fills the gel cavity

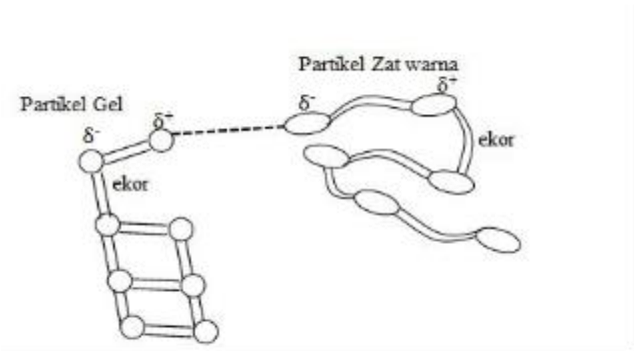

Figure 8. Illustration of the interaction between gel particles and color particles

4. Conclusion

Based on the research that has been done, it can be concluded that gelation preparation can be done using the sol-gel method with a gel in the form of a semi-solid which is not transparent to light. The solubility of methyl red in water-in-oil microemulsion gel for SDBS and pentanol water systems was the highest compared to the solubility in methylene blue samples. Methyl red has an average solubility of 0.00398 gr, while the average solubility value of methylene blue is 0.00375 gr.

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