

PROSIDING

SEMIRATA 2014

Bidang MIPA BKS-PTN-Barat

"Integrasi sains MIPA untuk mengatasi masalah pangan, energi, kesehatan, reklamasi, dan lingkungan"

IPB International Convention Center dan Kampus IPB Baranangsiang, 9-11 Mei 2014

BUKU 7

**KIMIA, BIOLOGI, GEOFISIKA
DAN METEOROLOGI, STEM**

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Kegiatan Seminar dan Rapat Tahunan Bidang MIPA tahun 2014 (Semirata-2014 Bidang MIPA) Badan Kerja Sama Perguruan Tinggi Negeri Wilayah Barat (BKS-PTN Barat) yang diamanahkan kepada FMIPA-IPB sebagai penyelenggara telah dilaksanakan dengan sukses pada tanggal 9-11 Mei 2014 di IPB International Convention Center dan Kampus IPB Baranagsiang, Bogor. Salah satu program utama adalah Seminar Nasional Sains dan Pendidikan MIPA dengan tema: *-Integrasi sains MIPA untuk mengatasi masalah pangan, energi, kesehatan, dan lingkungan*.

Dalam sesi pleno seminar telah disampaikan pemaparan materi oleh satu pembicara utama dan empat pembicara undangan yang berasal dari beragam institusi dan profesi. Dari sesi pleno ini, diharapkan peserta dapat menambah wawasan dan pemahaman tentang pengembangan dan pemanfaatan IPTEK, khususnya Bidang MIPA, sehingga sains dan pendidikan MIPA terus berkembang dan dapat berkontribusi nyata untuk kemajuan dan kemakmuran bangsa Indonesia.

Kegiatan yang tidak kalah pentingnya dalam seminar ini adalah sesi paralel karena telah memberi kesempatan kepada peserta untuk melakukan presentasi dan komunikasi ilmiah secara langsung dengan sesama kolega yang mempunyai minat yang sama dalam mengembangkan Sains dan atau Pendidikan MIPA. Dalam kegiatan sesi paralel ini dipresentasikan secara oral 592 judul makalah hasil penelitian yang disampaikan dalam 37 ruang seminar secara paralel, dan juga dipresentasikan 120 poster ilmiah. Dalam kegiatan komunikasi ilmiah secara langsung ini juga telah dimanfaatkan untuk menjalin jejaring agar lebih bersinergi dalam pengembangan Sains dan Pendidikan MIPA ke depannya. Supaya komunikasi ilmiah yang baik ini dapat juga tersampaikan ke komunitas ilmiah lain yang tidak dapat hadir pada kegiatan seminar, panitia memfasilitasi untuk menerbitkan makalah dalam bentuk **Prosiding**. Panitia juga tetap memberi kesempatan kepada peserta yang akan menerbitkan makalahnya di jurnal ilmiah, sehingga tidak seluruh materi yang disampaikan pada seminar diterbitkan dalam prosiding ini.

Dalam proses penerbitan prosiding ini, panitia telah banyak dibantu oleh Tim Reviewer dan Tim Editor yang dikoordinir oleh Ali Kusnanto yang telah dengan sangat intensif mencurahkan waktu, tenaga dan pikiran. Untuk itu, panitia menyampaikan terima kasih dan penghargaan. Panitia juga menyampaikan terima kasih dan penghargaan kepada seluruh penulis makalah yang telah merespon dengan baik hasil review artikelnya. Namun, panitia juga menyampaikan permohonan ma'af karena dengan sangat banyaknya makalah yang akan diterbitkan dalam prosiding ini, waktu yang dibutuhkan dalam proses penerbitan prosiding ini mencapai lebih dari empat bulan, dan penerbitan prosiding tidak dilakukan dalam satu buku tetapi dalam tujuh buku prosiding. Semoga penerbitan prosiding ini selain bermanfaat bagi para pemakalah dan penulis, juga dapat bermanfaat dalam pengembangan Sains dan Pendidikan MIPA.

Bogor, September 2014
Semirata-2014 Bidang MIPA BKS-PTN Barat

Dr. Ir. Sri Nurdiati, MSc.
Dekan FMIPA-IPB

Ence Darmo Jaya Supena
Ketua Panitia Pelaksana

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SOLUBILITY LIMITATION OF METHYL RED AND METHYLENE BLUE IN MICROEMULSIONS AND LIQUID CRYSTALS OF WATER, SDS AND PENTHANOL SYSTEMS

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ABSTRACT

Solubility of dyes in amphiphilic association structures of water, SDS and penthanol system (i.e. in the phases of microemulsions and liquid crystals) was attracted much interest due to its wide industrial and technological applications. This research was focused on understanding the solubility limitation of methyl red and methylene blue in microemulsion and liquid crystal phases. Experimental results showed that the highest solubility of methyl red was in LLC, followed by w/o microemulsion and o/w microemulsion, respectively, whereas the highest solubility of methylene blue was in w/o microemulsion, followed by o/w microemulsion and LLC, respectively. Hence, a chemical dynamics strongly played an important role in the solubility limitation of methyl red and methylene blue in microemulsions and liquid crystal phases.

Keywords: Amphiphilic association structure, liquid crystals, microemulsions, methylene blue

INTRODUCTION

The wide applications of surfactants in research and technology lead to the advanced study in the field of physical chemistry and material sciences[1]. Some thermodynamical aspects in terms of solubility has been studied and rapidly developed in this few decades[2]. Since it has many industrial and technological applications, such as: ink[3], paint[4], oil recovery[5], pharmaceutical[6], agricultural[7] and electronic industries[8]. Therefore, by understanding this field the chemical attractions and repulsions, or interactions could be open widely and the —grailll of chemical nature could be expressed in the simple meaning[9]. The aim of this research is to express the limitation of dyes solubility in microemulsions and liquid crystals of water, surfactant and cosurfactant system[10]. We focused on the three components system due to the applicability of such systems in many industries and technologies[11].

Solubility of dyes in microemulsions and liquid crystals could be used to probe

the microstructure of colloids association structures[12]. The homogeneity mixtures of microemulsions and liquid crystals systems[13] in macroscopic overview would bring a unique ability to dissolve dyes[14]. This phenomenon could be investigated at molecular level using *ab-initio* and chemical dynamics computations[15]. All interaction at molecular level could be expressed genuinely, however, in this research we proposed the solubility limitation of dyes in microemulsions and liquid crystals(especially in LLC) of water, sodium dodecyl sulphate and penthanol system.

EXPERIMENTAL SECTION

Materials and Methods

The following chemicals were used without further purification: nononic surfactant, SDS (sodium dodecyl sulphate) GR, nitric acid (70%) fuming, potassium hydroxide GR, n-penthanol and methylene blue were purchased from Merck KgaA, Germany, methyl red was obtained from Wako Pure Chemical Industries Ltd. The water was double distilled water (Rafi Medika) In addition, nitric acid (37%) was used as acid medium to adjust the water at pH = 4.5, and potassium hydroxide was used as the base medium to adjust the water at pH = 9.5.

Phase Diagram Preparation

The o/w and w/o microemulsion regions, as well as lamellar liquid crystal (LLC) and hexagonal liquid crystal (HLC) regions [from the water(pH of 4.5 and 9.5), SDS, and penthanol system], were determined by titration of SDS, penthanol with water to turbidity at room temperature (25° C). The solubility region was checked by long time observation, monitoring the turbidity of the samples both inside and outside the single phase regions. The phases in equilibrium with the microemulsion were identified as lamellar liquid crystal (LLC) and hexagonal liquid crystal (HLC) from its pattern when viewed between crossed polarizers in optical microscopes.

Solubility of Methyl Red and Methylene Blue in Microemulsions and Liquid Crystals

Solubility of methyl red, especially, in o/w and w/o microemulsions, lamellar liquid crystal regions, as well, were determined in the system of water (pH=4.5), SDS and penthanol. Whereas, solubility of methylene blue in o/w and w/o microemulsions and lamellar liquid crystals, was determined in the system of water (pH=9.5), SDS

and penthanol. In fact, the solubility of methyl red and methylene blue in HLC relatively low due to one dimensional periodicity structure. The procedure were: small quantity of methyl red/methylene blue were added gradually into a tube that was already filled with/by given composition of samples of interest. Stirring it, using vertexer. Hence, the solubility of methyl red/methylene blue was observed visually. Red and blue laser light were used to convince the visual appearance. In addition, the Hund Wezlar® Optical Polarizing Microscope was also used whenever needed. The addition was stopped when a very little precipitated of dyes showed, and saturated mixture was achieved.

RESULT AND DISCUSSION

Phase Diagram

Phase diagram of water (both of pH=4.5 and pH=9.5); SDS and penthanol system exhibits four main phase areas, i.e., o/w and w/o microemulsions, lamellar liquid crystal (LLC) and hexagonal liquid crystals (HLC), as shown in **Figure.1**.

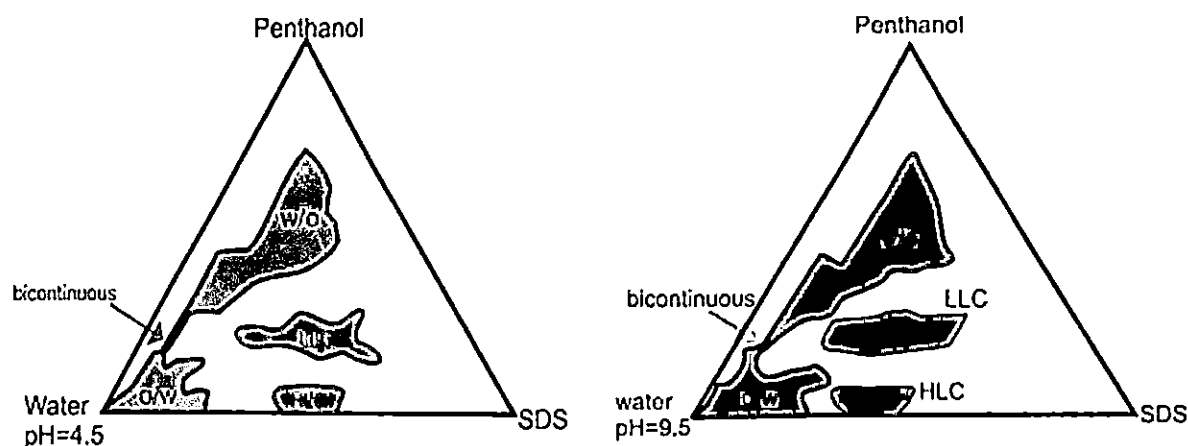


Figure. 1. Phase diagram of water, SDS and penthanol system which represents four phase areas; o/w and w/o microemulsions, lamellar and hexagonal liquid crystals. The bridge of w/o and o/w microemulsions lays bicontinuous phase. System of water, pH=4.5 (*left*) and system of water pH=9.5 (*right*).

In water at pH=4.5; SDS and penthanol systems, w/o microemulsion exhibited wide area in the middle of triangle along water and penthanol rich components. The coordinate positions were around 12-60% water; 6-35% SDS; and 30-70% penthanol content. Whereas o/w microemulsion exhibited the finger shape at water rich

composition. The coordinate positions were around 70-100% water; 0-25% SDS; and 0-14% penthanol content. In the middle of w/o and o/w microemulsions was a certain structure which united the two structures as a bridge which called bicontineous phase. This is a unique structure due to the o/w and w/o microemulsions mixed together to form a combination structure. Lamellar liquid crystal (LLC) was formed at the coordinate around 23-55% water; 24-60% SDS; and 14-25% penthanol content. Whereas hexagonal liquid crystal (HLC) was formed at the coordinate around 38-55% water; 40-57% SDS; and 1-7% penthanol content. The complete picture could be seen at the left side of **Figure.1**.

In water at pH=9.5; SDS and penthanol system, w/o and o/w microemulsions exhibited almost similar trends as well as water at pH=4.5. For w/o microemulsion, phase area lays on the middle of the triangle along water and penthanol rich components. The coordinate position were around 12-60% water; 6-50% SDS; and 30-77% penthanol content. Whereas o/w microemulsion exhibited the finger shape at water rich composition. The coordinate position were around 63-100% water; 0-26% SDS; and 0-14% penthanol content. In the middle of w/o and o/w microemulsions lays bicontinuous phase as well. Lamellar liquid crystal (LLC) was formed at the coordinate around 25-60% water; 19-49% SDS; and 18-28% penthanol content. Whereas hexagonal liquid crystal (HLC) was formed at the coordinate around 47-66% water; 28-48% SDS; and 0-8% penthanol content. The complete picture could be seen at the right side of **Figure.1**. Chemical structures of water, SDS and penthanol and cartoonic structures were represented in **Figure.2**.

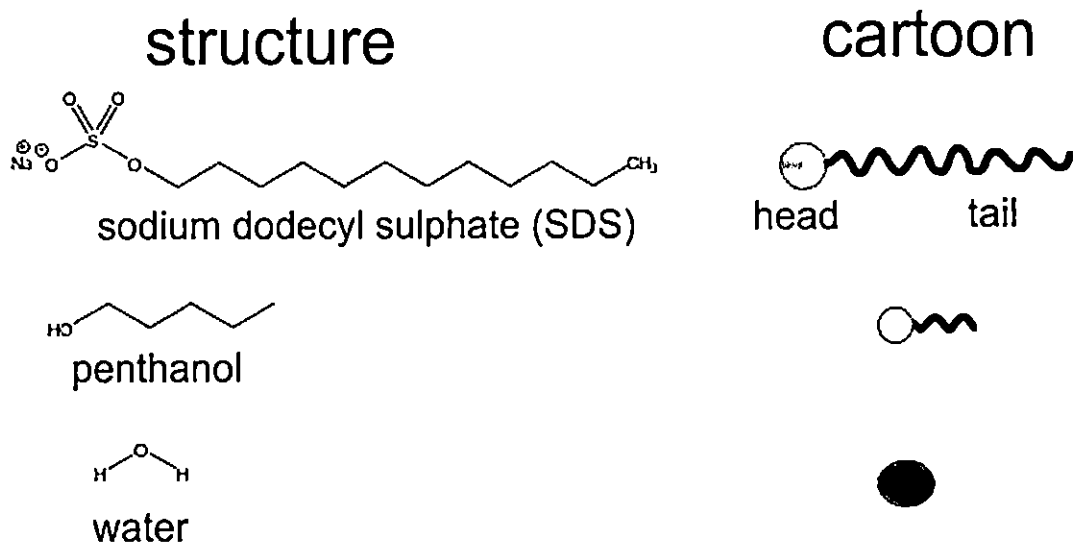


Figure. 2. Representation of chemical and cartoonic structures of SDS, penthanol and water. All three components arranged in given weight composition to formed phase diagram.

Both w/o and o/w microemulsions exhibited homogeneous clear solution which were stable in the long time periods at room temperature. The homogeneity was clarified using Hund-Wetzlar® optical polarizing microscope. Under microscope, the solutions was so clear with micro-spherical-dot (**msd**) distributed homogeneously throughout the solutions. The appearing of particles **msd** were measured in 40 μ m size in diameter. w/o microemulsion formed at rich oil content (poor water), whereas o/w microemulsion formed at poor oil content (rich water) in the triangle or phase diagram. Under polaroid-parafilm, both w/o and o/w microemulsions were inert in terms of light polarity rotation.

LLC exhibited homogeneous clear high viscous texture/substance which was stable under long period of time at room temperature. The rheology was measured under Hund-Wetzlar® optical polarizing microscope and it formed a layer structures. LLC formed a series of **msd** horizontally and there was a space among the layers. In addition, HLC exhibited a two dimensional and highly homogeneous viscous texture/substance which was difficult to mixed under thermolyne® mixer. The difficulty was not easy to resolve. Under parafilm apparatus, the HLC phase was rotated the polarization light. The representative formation of o/w and w/o microemulsions could be simplified in cartonic form as shown in **Figure. 3**.

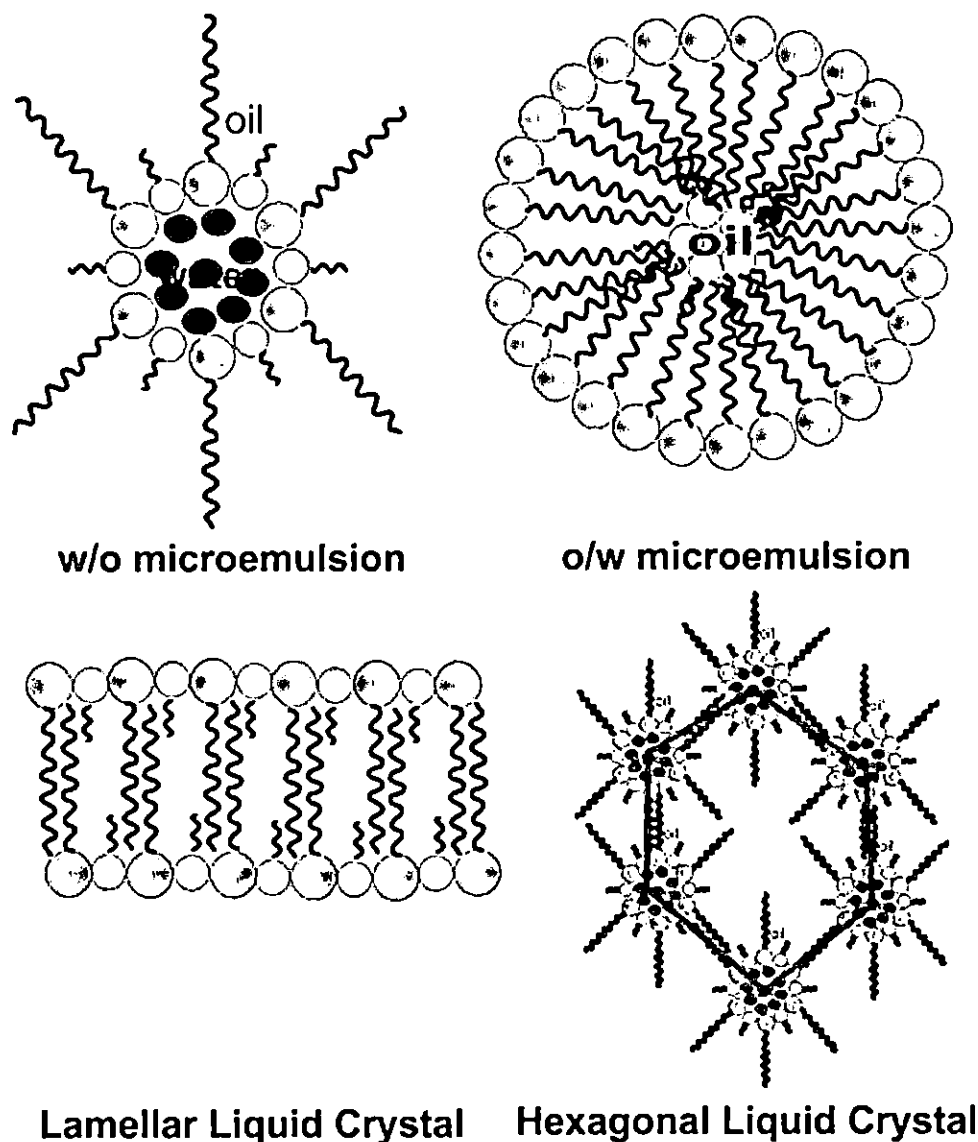


Figure. 3. Cartoonic representation the two dimensional cross section of w/o and o/w microemulsions and lamellar and hexagonal liquid crystals. Experimental model for phase formation of phase diagram.

Solubility of Methyl Red and Methylene Blue in Microemulsions and Liquid Crystals

Solubility of methyl red was determined for w/o and o/w microemulsions and LLC phase for system of water at pH=4.5, SDS and penthanol, whereas solubility of methylene blue was determined for w/o and o/w microemulsions and LLC phase for system of water at pH=9.5, SDS and penthanol. We notice that, HLC phase for both system was not determined due to the technical problems. The result was tabulated in **Table 1**.

Table 1. Solubility Data for Methyl Red in Microemulsions and Lamellar Liquid Crystal of Water pH=4.5, SDS and Penthanol System

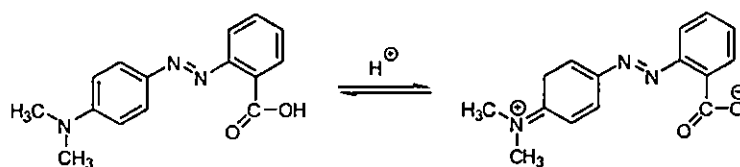
Phases	Solubility of Methyl Red in mg
O/W microemulsion	0.06
W/O miroemulsion	0.13
LLC	0.70

The solubilisation of methyl red in LLC was the highest compared to w/o and o/w microemulsions in the water at pH=4.5, SDS and penthanol system (data Table 1). In contrast, the solubilisation of methylene blue in LLC was the lowest compared to o/w and w/o microemulsions (data Table 2).

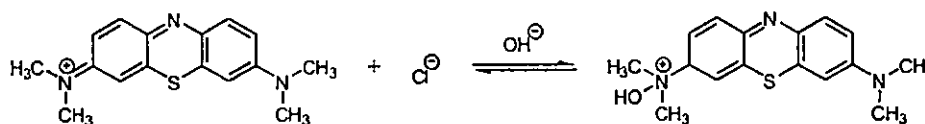
Table 2. Solubility Data for Methylene Blue in Microemulsions and Lamellar Liquid Crystal of Water pH=9.5, SDS and Penthanol System

Phases	Solubility of Methyl Red in mg
O/W microemulsion	0.38
W/O miroemulsion	0.46
LLC	0.27

The chemical structure of methyl red and methylene blue and cartoonic



methyl red



methylene blue



structures represented in Figure. 4.

Figure. 4. Chemical and cartoonic structures for methyl red (upper) and methylene blue (lower) in their chemical properties condition (acid and basic).

Using such model as represented in **Figure.4** we could made a model for chemical interaction for methyl red and methylene blue in the association structures. This interaction model could be pictured as **Figure.5** and **Figure.6**.

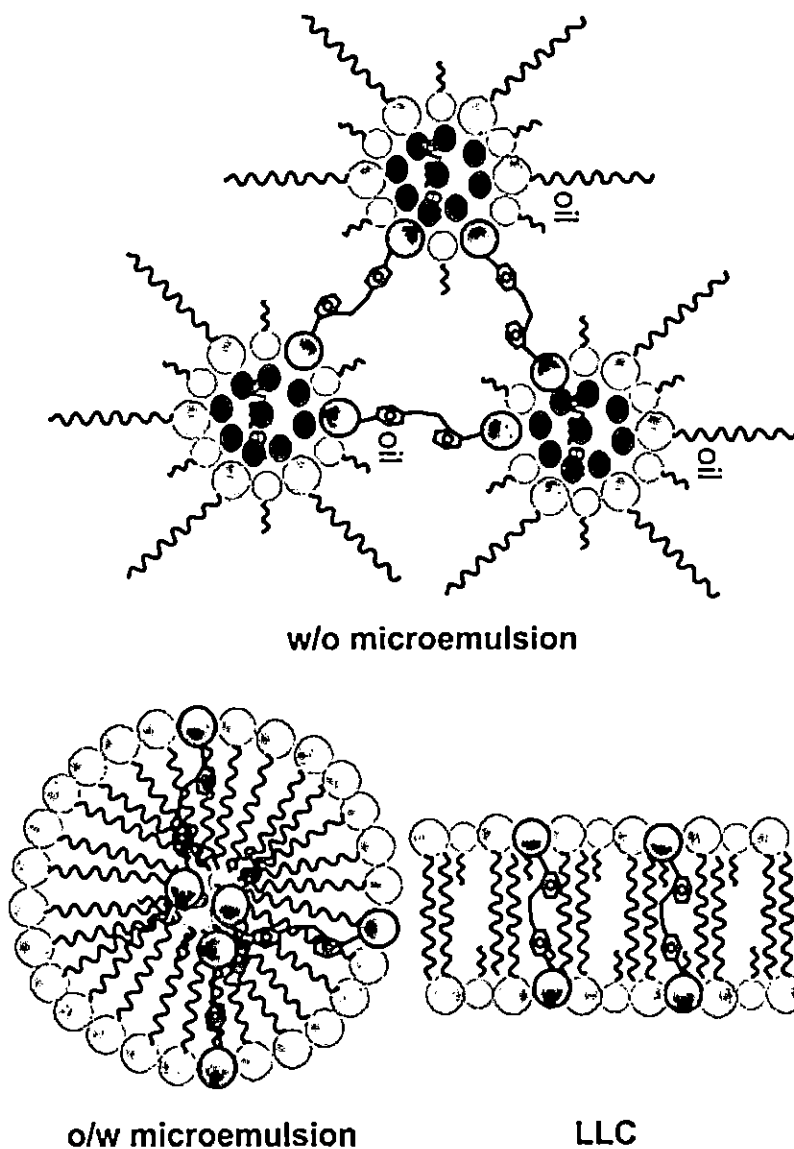


Figure. 5. Chemical interaction between methyl red in the association structures

Solubilisation of methyl red in LLC is more preferable due to the maximum interaction of polar head groups in LLC structure. Herein, the methyl red tail groups arranged in parallel position to the oil, this state associated with main LLC structure. Nevertheless, the solubility of methyl red would maximize in this model. In w/o microemulsion, the methyl red molecules arrange the **msd** structures associated together to form compact structures to help the dilution of methyl red. However, in o/w microemulsion, the existence of methyl red tends to break the globular structures. This process would not easy to be done, due to the associative forces of o/w microemulsion structure. Therefore, at o/w microemulsion a limited number of

methyl red would dissociated in structure. The complete picture of the solubilization process could be seen in **Figure. 5**.

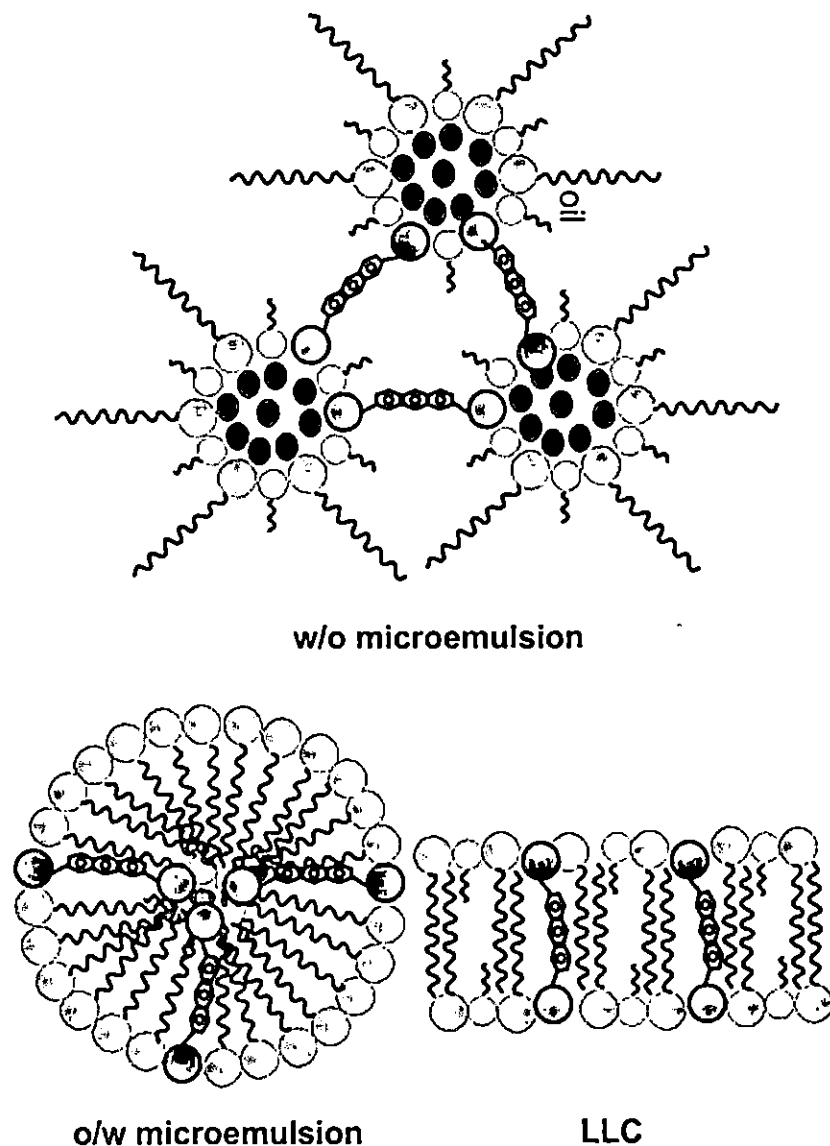


Figure. 6. Chemical interaction between methylene blue in the association structures

The solubilisation of methylene blue in association structure were unique, due to the methylene blue could almost be diluted in the number of proportions. As we could seen in **Figure.6**, the solubilisation of methylene blue in w/o microemulsion were preferable since the existence of methylene blue would associate **msd** to combined each other, so the chemical tension would be minimized. In addition, the chemical structure for methylene blue, a bit short in comparison to methyl red, so the chemical potentials of methylene blue could break the o/w structures and it could explained the high solubility of methylene blue in o/w structures. The limited solubility of methylene blue in LLC could be explained by: the short carbon chain would force

the layer structures to distort in the given position where the methylene blue associates. Because of the tension, the solubility of methylene blue was restricted.

CONCLUSIONS

In this research we have figured out the association structures for system of water at pH=4.5, and pH=9.5; SDS and penthanol. Area of w/o, o/w microemulsion, lamellar liquid crystal and hexagonal for water at pH=4.5 system were at coordinate positions around 12-60% water; 6-35% SDS; and 30-70% penthanol: 70-100% water; 0-25% SDS; and 0-14% penthanol: 23-55% water; 24-60% SDS; and 14-25% penthanol: 38-55% water; 40-57% SDS; and 1-7% penthanol contents, respectively. Whereas Area of w/o, o/w microemulsion, lamellar liquid crystal and hexagonal for water at pH=9.5 system were at coordinate positions around 12-60% water; 6-50% SDS; and 30-77% penthanol : 63-100% water; 0-26% SDS; and 0-14% penthanol : 25-60% water; 19-49% SDS; and 18-28% penthanol : 47-66% water; 28-48% SDS; and 0-8% penthanol contents, respectively.

The limited solubility for methyl red take place in o/w microemulsions since methyl red need an extra potential to break the msd structure in order to put methyl red molecules in. Whereas, the limited solubility for methylene blue take place in LLC due to the short carbon chain would force the layer structures to distort in the given position where the methylene blue associates.

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