FORMATION AND STABILITY OF MICRO-EMULSION USING NONIONIC SURFACTANT AND CATIONIC POLYMER SYSTEMS

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ABSTRACT

The formation of micro-emulsion has been studied in water phase/nonionic surfactant/oil phase system and water phase/mixed cationic polymer-nonionic surfactant/oil phase system using emulsification addition of water phase to a surfactant in oil phase. In this method water was added dropwise to a solution of mixed surfactant in oil phase at room temperature and 8000 rpm of mixing rate. The droplet size and stability were determined as a function of amount of water, oil, and surfactant. Among of tested samples the stability could be arranged as PC 1 > PC 2 > GM > PE but the droplet size was on the contrary as PC 1 < PC 2 < GM < PE.

Key words: emulsion, nonionic surfactant, cationic polymer, stability

INTRODUCTION

When water, oil and a surfactant are mixed, the surfactant rests at the water-oil interface. These systems depending on their stability are called emulsions or micro-emulsions, which are thermodynamically stable. Although, the properties for an emulsion and a micro-emulsion are different, both obey the same principle: they try to form enough interface for preventing the polar non-polar solvent contact. Micro-emulsions are micro-structured, thermodynamically stable isotropic mixtures of oil, water and surfactant, frequently in combination with a co-surfactant. The sizes of these structures are in the range of a few hundreds of nanometers. The aqueous phase may contain salt and/or other ingredients, and the oil may actually be a complex mixture of different hydrocarbons and olefins. Glycerol monooleate can be function as co-surfactant.

Micelles and micro-emulsions are liquid dispersion containing surfactant aggregates. In micellar dispersions, the aggregates are made of surfactant only and are usually dispersed in water. In micro-emulsions, the aggregates are much larger: they have large liquid cores [oil in water (o/w) micro-emulsion and water in oil (w/o) micro-emulsion] surrounded by a surfactant monolayer that stabilizes the dispersion. Surfactant molecules do not always associated into micelles, and in some cases, do not form closed structures. In application amount of surfactant must be added higher than its critical micelle concentration (CMC). CMC is concentration the surface becomes completely loaded with surfactant and any further additions must arrange as micelles.

Nonionic surfactants are a surfactant with no charge group. Polymers are long chain giant molecules assembled from smaller units (monomers). There are natural polymers such as: silk, proteins, rubber, carbohydrates, cellulose, chitin-chitosan, and also DNA. Chitosan is a natural polymer obtained by the hydrolysis of chitin, a native polymer present in prawns and crabs shell. Chitosan can be reacted with 3-chloro 2-hydroxy propyl trimethyl ammonium chloride to form cationic water-soluble chitosan.

Polymerizable surfactants have been used in a variety of application including capturing the structure of spherical micelles and as a stabilizer in emulsion. These functions are caused by polymer-surfactant interaction. There are two types of interactions, i.e. electrostatic and hydrophobic interactions. The electrostatic interactions can be occurred if the polymer and the surfactant are oppositely charged. And the hydrophobic interactions can be occurred between the hydrophobic parts of both the polymer and surfactant.

The presence of polymeric chains induces the formation of micelles. The presence of similarities between the surfactant and the polymer attract the surfactant molecules to certain positions in the polymer. The main attraction forces are still hydrophobic interactions. The same mechanism and entropy balance hold for micellization in presence of polymer. Usually the same aggregate size and aggregation number. The presences of oppositely charged species do enhance interaction.

Applications of polymer-surfactant mixtures, in this case polymers are added to surfactants, are in order to control the phase behavior (e.g. to solubilize...
water insoluble polymers) and to control the interfacial properties (e.g. to stabilize suspensions which depends on a complex interplay between different pair interactions. Addition of a polymer can either remove a surfactant from a surface or enhance its adsorption to a surface). The polymer-surfactant mixtures are also can be used to achieve a suitable rheology, because of their thickening and gelation effect. Moreover, the polymer induced micellization lead to a lower surfactant free molecules concentration and activity (e.g. in skin formulations, free surfactant molecules cause skin irritation).

EXPERIMENTAL SECTION

MATERIALS
Water phase consist of water, propylene glycol, glycerine, and polyethylene glycol 4000. Oil phase consist of virgin coconut oil, ethanol, methyl parahydroxy benzoate, and perfume. Virgin coconut oil was prepared by the Division of Environmental Technology, Research Center for Chemistry, Indonesian Institute of Sciences. There are several types of surfactant that used in this experiment, such as polyethylene glycol 400 monooleate (PEG400MO), glyceril monostearate (GMS), and cationic water-soluble chitosan (CWSC). All of the surfactants were synthesized according to the previously published method.

METHOD

Critical micelle concentration
Prior to emulsion formation, CMC should be determined. Determination of CMC was carried out by preparation of mixture using surfactant of various concentrations. Surface tension of each mixture was measured using surface & interfacial tension torsion balance.

Preparation of Emulsion
The emulsions were prepared by homogenizing surfactant and oil phase. Water phase was added dropwisely. Preparation of emulsions was carried out at room temperature, 8000 rpm of mixing rate for 5 minutes. The samples were prepared with variations of composition of the amount and type of surfactants (Table 1). Sample PE was the emulsion, which was prepared by usage of PEG400MO as a surfactant. Sample GM was the emulsion, which was prepared by usage of mixture of PEG400MO and GMS as surfactants. And sample PC1 and PC2 were the emulsions, which were prepared by usage of mixture of PEG400MO and cationic water-soluble chitosan as surfactants.

Droplet size
The droplet size of emulsion were measured by Optical Microscope from Carl Zeiss type Axio Imager M1.

Stability
The emulsion stability was tested using centrifuge type Kokosan H-103N series at 3000 rpm for 10 minutes. Emulsion stability was indicated by homogenous phase without separated phase.

RESULT AND DISCUSSION

The result for critical micelle concentration (CMC) depending on surfactant concentration and surface tension are shown in Figure 1. The addition of surfactant to the water had substantial effect on surface tension. However, conclusion should be taken because it is reported that amount of surfactant must be added higher than its critical micelle concentration (CMC). In this experiment, log CMC PEG 400 MO was -3.68, so its mean CMC value was 2.09 x 10^-4 mol/L.

Table 1. Composition of samples (in gram)

<table>
<thead>
<tr>
<th>Ingredient (g)</th>
<th>PE</th>
<th>GM</th>
<th>PC 1</th>
<th>PC 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water phase</td>
<td>84.1</td>
<td>84.1</td>
<td>84.1</td>
<td>84.1</td>
</tr>
<tr>
<td>Oil phase</td>
<td>10.9</td>
<td>10.9</td>
<td>10.9</td>
<td>10.9</td>
</tr>
<tr>
<td>PEG 400 MO</td>
<td>5</td>
<td>2.5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>GMS</td>
<td>-</td>
<td>2.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CWSC</td>
<td>-</td>
<td>-</td>
<td>1</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Figure 1. Critical micelle concentration (CMC) Polyethylene glycol 400 monooleate
Type of emulsion that made in this work was oil-in-water (o/w) emulsion. The water phase had more of quantity than oil phase for each of formulas. The droplet size of emulsion was analyzed using optical microscope (Table 2).

Figure 3a-d and table 2 showed the condition of emulsion based on the formula. PE emulsion consists of PEG400MO as a single surfactant. The droplet of emulsion was not observed in the micrograph (Figure 3a). This was due to the small size of the droplet. Micelles of surfactant spread in medium phase.

In the emulsion formula GM, two kinds of nonionic surfactants PEG400MO and GMS were mixed with the same ratio. The emulsion droplets were observed from the micrograph in Figure 3b. The size of emulsion droplet was relatively bigger than formula PC 1 and PC 2.

Abe M et al. said that polymerizable surfactants have been used in a variety of application including capturing the structure of spherical micelles and as a stabilizer in emulsion. In this case, cationic water-soluble chitosan (CWSC) was a polymerizable surfactant that has been used in PC 1 and PC 2 emulsion formula (Scheme 1). Micrograph in figure 3c and Figure 3d and table 2 showed that droplet size of PC 1 was a little smaller than PC 2. This condition indicates CWSC induces the formation of micelles. The distribution of droplet size of the formula used CWSC as surfactant showed better than the other formulation. The interaction between cationic polymer with non-ionic surfactant was obeyed in this formula, and caused the smaller size and better droplet distribution.

Emulsion instability results from physical processes, i.e. flocculation, coalescence, Oswald 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 droplet. Centrifugation is physically process to determine emulsion stability.

Based on Table 3, PC 1 was more stable than the others. The conditions of emulsion before and after centrifuge were physically same. This condition is same with formula PE emulsion, although the droplet emulsion in PE was not observed in micrograph. Creaming at the top and sedimentation in the bottom of GM indicated that the emulsions were relatively unstable. Sedimentation in PC 2 emulsion was also formed. Too much amount of cationic polymer affected in the unstability of emulsion. The interaction between cationic polymer with non-ionic surfactant was destroyed by the existing of over capacity cationic polymer.

CONCLUSION
Surfactants, water phase and oil phase were needed to form emulsion. Combination of PEG400MO with cationic polymer such as cationic water-soluble chitosan (CWSC) produced a stable emulsion with small droplet emulsion (micro-emulsion). The increase of CWSC in emulsion formulation caused unstartability of the emulsion.

ACKNOWLEDGEMENTS.
Support from the Indonesian Toray Scientific Foundation (ITSF) Science and Technology research Grant and DIPA LIPI research grant are greatly acknowledged. The authors acknowledge droplet size of emulsions using optical microscope from Carl Zeiss type Axio Imager M1 supported by PT. Vanadia Utama, Jakarta.

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