Faculty of Resource Science and Technology

SYNTHESIS AND CHARACTERIZTION OF NON-IONIC SURFACTANT

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SYNTHESIS AND CHARACTERIZATION OF NON-IONIC SURFACTANT

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DECLARATION

I hereby declare that portion of the work referred in this thesis are submitted in support of an application for another degree or qualification to this or any other university or institution of higher learning.

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List of Abbreviations

CMC	Critical Micelle Concentration
CP	Cloud Point
DMS-D^6	Deuteron chloroform
EO	Ethylene Oxide
EON	Ethylene Oxide Number
EPA	Environmental Protection Agency
FNU	Formazin Nephelometric Unit
FTIR	Fourier Transform Infrared Spectroscopy
FTU	Formazin Turbidity Unit
HLB	Hydrophilic-Lipophilic Balance
^{1}H NMR	Proton Nuclear Magnetic Resonance
MHz	Mega Hertz
mL	Millilitre
Mm	Millimetre
MPS	Multi Parameter Scanning
MW	Molecular Weight
NTU	Nephelometric Turbidity Unit
PEG	Polyethylene glycol
Surfactant	Surface Active Agents
TMS	Tetramethylsilane
UV-Absorption	Ultra-Violet Absorption Spectroscopy

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Synthesis and Characterization of Non-ionic Surfactant

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ABSTRACT

Non-ionic surfactant derived from Kojic acid was synthesized and analyzed. The synthesis of non-ionic surfactant involved the esterification of stearic acid-polyethylene glycol ester with Kojic acid. The structure of the synthesized non-ionic surfactant was confirmed by using FTIR, ^{1}H NMR and ^{13}C NMR. The properties of synthesized compound such as critical micelle concentration (CMC), cloud point, wetting time, foaming and foam stability, pH value and also emulsion stability was investigated. The synthesized compound showed high value of cloud point (91^{o}C) and wetting time (139 seconds) in addition to their low CMC at 0.0008M. As the number of ethylene oxide chain units in the synthesized compound higher, the foaming and foam stability also higher, which is 71.67 %. The synthesized compound has pH value of 5.45 where the common non-ionic surfactant posses pH value at the range 3 to 12. Moreover, the synthesized non-ionic surfactant showed lower emulsification power (25 seconds) that makes them useful for wide ranges of applications.

Keywords: Non-ionic surfactant, Kojic acid, CMC, cloud point, wetting time, foam and foam stability, pH value, emulsion stability.

ABSTRACK

Surfaktan bukan ionik yang diperolehi daripada asid Kojic telah pun disintesis and dianalisis. Sintesis surfaktan bukan ionik melibatkan pengesteran asid stearik-polietilena glikol ester dengan asid Kojic. Struktur surfaktan bukan ionik yang telah diperolehi, disahkan dengan menggunakan FTIR, ^{1}H NMR dan ^{13}C NMR. Ciri-ciri sebatian surfaktan yang dikaji adalah seperti kepekatan kritikal misel (CMC), titik kekeruhan, tempoh basahan, pembuihan dan kestabilan buih, nilai pH dan juga kestabilan emulsi. Hasil kajian menunjukkan surfaktan bukan ionik mempunyai nilai titik kekeruhan (91^{o}C) dan tempoh basahan yang tinggi (139 saat) di samping nilai CMC yang rendah, iaitu 0.0008M. Pembuihan dan kestabilan buih meningkat dengan bilangan unit rangkaian etilena oksida sebanyak 71.67%. Sebatian yang disintesis mempunyai nilai pH 5.45 di mana biasanya surfaktan bukan ionik menunjukkan nilai pH di antara 3 hingga 12. Tambahan pula, surfaktan bukan ionik menunjukkan kuasa pengemulsian yang rendah sebanyak 25 saat, yang membolehkan ianya sangat berguna dalam pelbagai aplikasi.

Kata kunci: Surfaktan bukan ionik, asid Kojic, kepekatan kritikal misel, titik kekeruhan, tempoh basahan, pembuihan dan kestabilan buih, nilai pH, kestabilan emulsi.

1.0 INTRODUCTION

Surfactants also known as surface-active agents or detergents are one of the groups of most popular chemical available in our daily life application (Dominguez *et al.*, 1997). Surfactants are chemical composition that consists of a hydrophilic head and a long chain hydrophobic tail. Depending on the hydrophilic head group, surfactants can be categorized into four types including anionic, cationic, amphoteric and non-ionic surfactant (Balouch, 2009). Surfactants have found widely uses in various applications include detergents, shampoos, crude oil recovery enhancers, cosmetics, chelating agents and also antimicrobial agents.

30% of the worldwide surfactants consumption is attributed by non-ionic surfactants (Schmitt, 1992). When compared to anionic surfactants, non-ionic surfactants have more tolerant in the hardness of waters and also more effective in the removal of oily soil from fabrics. Non-ionic surfactants do not ionize in aqueous solution because of their non-dissociable hydrophilic group types such as ether, alcohol, amide, phenol and ester. The characteristics of non-ionic surfactants are low-foaming products, good cool water solubility and also low critical micelle concentration (CMC), which makes them more effective at low levels. The polyethylene oxide family, structure and also dynamical properties of micelles play an important role in their applications (Wolszczak and Miller, 2002).

According to Ahmed (2010), non-ionic surfactants can be produced either by the polycondensation process of ethylene oxide (EO) of hydrophobic organic compounds containing active hydrogen under alkaline conditions or by esterification reaction of various raw materials which are plants based and renewable resources such as plant oil with polyethylene glycol fatty ester.

In this study, the starting materials used to produce the environmentally friendly non-ionic surfactants are polyethylene glycol (PEG), stearic acid and also kojic acid. According to Feng *et al.* (1996), PEG is a unique neutral water soluble polyether due to its special ability to repel proteins without denaturing them; extremely high water solubility, and also availability in various molecular weights. The application of PEG as an organ preservation proven PEG is relatively nontoxic and harmless to cellular system. PEG is also known to associate with membrane phospholipids head group as large quantities of PEG can be absorbed by the membranes.

Gunstone (1996) defined fatty acids as a long straight-chain compounds consist of an even number of carbon atoms in their molecules. The chain length of fatty acids commonly ranges from two to over 80 carbon atoms. The lipophilic group of fatty acids is very crucial in their applications of surfactants for cosmetics, pharmaceuticals, personal hygiene products and also food products (Cotton and Wilkinson, 1988). They can be categorized into saturated and unsaturated fatty acids. The most common fatty acids which are natural triglycerides are palmitic acid, stearic acid, oleic acid, linoleic acid and linolenic acid. Stearic acid, which also known as octadecanoic acid is a widely distributed saturated fatty acid consist of 18 carbon atoms. Stearic acid is the main compound of the tallow of ruminant animals (about 5-40%) and found excess in vegetable tallow (solids fats of vegetable origin) such as shea butter (45%) and cocoa butter (30-35%) (Gunstone, 1996). The –OH group present in the polyethylene oxide end chain undergo esterification process with other compound that consist –OH group at the end chain such as fatty acid, which would produce an important family of non-ionic surfactants.

Kojic acid is a natural product origin that has been isolated from variety species of microorganisms such as *Penicillium*, *Aspergillus* and *Gluconoacetobacter* (Novotny *et al.*, 1999). The chemical name of kojic acid is 5-hydroxyl-2-hydroxymethyl-4-pyrone, which is widely used in the cosmetic products as a skin whitening agent in the concentration of 1% (Cabanes *et al.*, 1994). The application of kojic acids are quite wide as they are commonly used as a tyrosinase inhibitor (to inhibit melanin formation), a metal chelating agent, an antioxidants for fats and oils, as a skin whitening agents (in cosmetics) and also intermediate in some synthesis (preparation of esters derivative such as kojic oleate and kojic stearate). Moreover, some people used kojic acid in the prevention of discoloration of crustacean, meat and fresh vegetables (Cabanes *et al.*, 1994; Jarchem Industries, 2000). Nowadays, many pharmaceutical sectors used kojic acids as an intermediate for the manufacture of chemicals.

Thus, the objectives of this study are:

1. To synthesis the non-ionic surfactant derived from kojic acid
2. To investigate the properties of synthesized non-ionic surfactants such as critical micelle concentration (CMC), cloud point, wetting time, foaming and foam stability, pH and emulsion stability.

2.0 LITERATURE REVIEW

2.1 Surfactant

Surfactant is chemical compound that has globally dominates in the industrial product compositions and has being formulated in high-performance applications such as electronics manufacturing, precision optic coatings and also pharmaceutical delivery systems (Zoller and Sosis, 2009). Other uses of surfactant are laundry detergents, industrial and institutional cleaning products, food-grade emulsifies and as a plastic mold release agents.

2.2 Non-ionic Surfactant

Non-ionic surfactant is types of surfactant that when dissolve in aqueous solution, they do not produce any ions (Jean-Louis, 2002). As a result, they are very compatible with other types of surfactants when mixed together, as mainly found in commercial products. Moreover, they can be used in high salinity or hard water and less sensitive to electrolytes. Generally, non-ionic surfactants are good wetting agents, emulsifiers and also better detergents. However, only certain types of non-ionic surfactants have a good foaming property.

Today, many industries especially pharmaceutical industry demand a more environmental friendly surfactants as the awareness about the effects of surfactants on the environment are increased. Some traditional surfactants have toxic effects on microorganisms by causing disruption which leads to cellular lysis (Taban, 2013). The most important factor in the environmental acceptance of the surfactants is the biodegradability property. There are many natural products that can be used as the starting materials for the manufacturing the non-ionic surfactants. The natural raw materials can join to the special structures in the surfactant which may lead to the creation of new functional properties that can be a better alternative for the traditional surfactants.

The world dominated types of non-ionic surfactants in the market is polyethoxylated types, which those that consist of polyethylene glycol chain result from the poly-condensation reaction of ethylene oxide on the hydroxyl or amine group (Jean-Louis, 2002). The poly-condensation reaction produces different products depending on the relative acidity of the R-XH molecules and its ethoxylated counterpart of RX-CH_2CH_2-OH. In all commercial products of surfactant, the distribution of ethylene oxide number (EON) varies in a mixture of different oligomers. In order to create the non-ionic surfactants that provide good solubility in water, the ethylene oxide groups must be at least 4 – 5 groups with the lipophilic group of at least C_{13} alkyl. In addition, the properties of the non-ionic surfactants would change as the factors such as temperature and changes in formulations would affect the relationship between the polyethylene oxide chain and water-oil physicochemical environment.

2.2.1 Synthesis of non-ionic surfactant

Non-ionic surfactant can be synthesized by various methods depending on types of starting materials used. Twenty percent of non-ionic surfactants are produced from the esterification reaction between fatty acid with the polyethylene oxide chain end group or polyalcohol that contain hydroxyl (–OH) group in the molecule (Jean-Louis, 2002). The products of esterification reaction have become an important family of non-ionic surfactants due of their excellent interaction with biological tissues that make them compatible for pharmaceuticals, cosmetics and foods products. In addition, the esterification reaction of fatty acids and other natural carboxylic acids such as abietic acids will produced non-ionic surfactants that are cheapest than others. But, these types of surfactant do not produce foam and will hydrolyze when used at alkaline condition.

Ahmed (2010) discovered that non-ionic surfactants can be synthesized by the addition of ethylene oxide of hydrophobic organic compounds consist of active hydrogen with the presence of suitable catalyst (basic catalyst such as KOH, $Ba(OH)_2$, $Sr(OH)_2$, BF_3 and $SnCI_4$). His synthesis of a novel series of non-ionic surfactants used alkyl (octyl, decyl and dodecyl; C_8, C_{10} and C_{12} respectively) benzene sulphonyl chloride as a starting materials. The reaction started by reacting the alkyl (C_8, C_{10} and C_{12}) benzene sulphonyl chloride with ethanolamine to produces a mixture of oligo(poly)ethylene glycol ethers. The ethylene oxide were then reacted with oligo(poly)ethylene glycol ethers in the presence of different catalysts (base KOH, Lewis acid $SnCl_4$ and K10 clay) to produce different moles of non-ionic surfactants. The properties of non-ionic surfactants depends on the ethylene oxide added (average degree of ethoxylation), types of starting material and also types of catalyst used. The surface activity, biological activities and biodegradability of the synthesized compounds also been investigated. He concluded that all the synthesized compounds have excellent surface and biological activities as well as good biodegradability properties.

However, due to the increasing awareness of surfactants impacts on the environment, the demands for the more environmentally friendly surfactants products were increased. As the solutions to those problems, many chemical industries focusing towards the creation of more eco-friendly surfactants derived from renewable resources and majority of the eco-friendly surfactants are the non-ionic surfactants (Negm *et al.*, 2012).

The environmentally friendly non-ionic surfactant can be synthesized by using the natural and renewable raw material that posses great environmental compatibility and highly biodegradable. Negm *et al.* (2012) synthesized non-ionic surfactant that derived from tannic acid, which is natural product that present in several plant species. The esterification reaction between tannic acid and polyethylene glycol fatty acids with varies number of ethylene glycol units produced environmentally friendly non-ionic surfactants. The properties such as surface tension, critical micelle concentration (CMC) and emulsification power were determined. They concluded that tannic acid derived surfactants shows good surface activity in additions to their low CMCs.

Study by El-Dougdoug *et al.* (2000) produced surface active agents from malic acid by the process of esterification with acyl chloride of (palmitic, oleic, stearic, linoleic and mixed fatty acids of rice bran oil (RBO) with the presence of pyridine as catalyst forming a compound which are converted to anionic disodium salt. The prepared α-acyl-oxysuccinic acid derivatives was oxypropenoxylated with different moles of propylene oxide (n = 2, 4, 6 and 8) and the synthesized compounds were then converted into non-ionic surfactant with two terminal amide oxide group as molecular aggregation and also surface active agents in aqueous solution. The synthesized compounds have shown excellent surface active property.

Lakhrissi *et al.* (2011) synthesized a series of non-ionic surfactants based on bis-galactobenzimidazolones by grafting alkyl bis-benzimidazolone moieties as hydrophobic tail on hydroxypropyloxygalacto-pyranose units as hydrophilic heads. Benzimidazolones are an important heterocyclic compounds that have pharmaceutical and biological importance. These types of non-ionic surfactant is a sugar-based surfactants that shown low toxicity and excellent biodegradability. Moreover, they have wide applications especially in microbiology, biotechnology, pharmaceutical and also biomedical.

The synthesis and evaluation of some surface active agents containing heterocyclic unit from the long chain fatty amine was done by Eissa (2007). She used N-Heptadecanoyl-3-(4-oxo-4H-benzo[d] oxazin-2-yl) – acrylamide as precursor to create propenoxylated non-ionic surface active agents that contain heterocyclic such as thiazole, triazole, benzoxazine, quinazoline, triazine, and oxazine. Spectroscopic tools such as IR, ^{1}H NMR and mass spectroscopy were used to confirm the structure of the prepared compounds. Physical properties such as surface and interfacial tension, cloud point, foaming height, wetting time, emulsification power, critical micelle concentration (CMC) as well as antimicrobial and biodegradability properties were also investigated. She concluded that the novel groups of non-ionic surface active agents that have heterocyclic moieties have dual functions, which are as antimicrobial and surface active agents with excellent wetting and emulsifying properties.

Taban (2013) have done a research on the preparation, characterization and evaluation of non-ionic surfactants that are prepared from olive oil. The starting material used were taken from two different sources which are the commercially available olive oil from Aldrich with different hydrocarbon chains and the crude fatty acid extracted from olive oil through hydrolysis process. He also manufactures the non-ionic surfactants with different head groups such as triethanolammonium chloride, pyridiunium chloride and trimethyammoniumm chloride. The physiochemical properties (surface tension, critical micelle concentration, Kraft point, cloud point, foaming height, wetting power and emulsification power), biodegradability and antimicrobial activity of the synthesized non-ionic surfactants were studied. The synthesized compounds have proven to be acceptable in term of biodegradability as they inhibited the growth of fungi and also gram positive and gram negative bacteria.

The glycerol derived ester-based surfactants have received much attention as they possess the good toxicological and ecological properties and interesting interfacial behaviour (Kandeel, 2011). They have known to be important surfactants with low hydrophilic-lipophilic balance (HLB) value because of the specific hydrophilic and hydrophobic units present in their structures provide useful applications as benign and environmentally friendly water-in-oil emulsifiers.

Kandeel (2011) has done a study on the synthesis of series of novel glycol-based non-ionic surfactants from the trans esterification of various long chain fatty acid methyl ester with glycerol ester of dibasic acid (succinic acid and adipic acid). The properties such as surface tension, critical micelle concentration, surface excess at air water interface and minimum surface area (A_{min}) have been studied for the synthesized products. The effect of hydrophilic and hydrophobic moieties on their physicochemical properties were also been studied. The HLB value was determined by the molecular weight of the fatty acids. Thus, as the molecular weight of fatty acid decrease, the hydrophilic nature of the ester will be increase which would lead to the increasing of HLB values. Moreover, an increase in the number of fatty acid units that react with the glycerol ester of dicarboxylic acids will result in a more lipophilic product. His study concluded that the synthesized glycerol-based non-ionic surfactants exhibit excellent surface-activity and known to be better non-ionic surfactants compared to widely use non-ionic surfactants such as octyl phenol (9-10) ethylene oxide condensate.

In this study, we synthesize non-ionic surfactant derived from Kojic acid (raw materials of sago waste and fungus). The reaction involved the esterification of stearic acid-polyethylene glycol ester with Kojic acid. The synthesized compound was confirmed by FTIR, ^{1}H NMR and ^{13}C NMR. The properties such as CMC, cloud point, wetting time, foaming and foam stability, pH and emulsion stability were investigated. This study aim to synthesize non-ionic surfactant that is more environmentally friendly, to reduced the impacts of surfactant to the environment.

2.3 Critical Micelle Concentration (CMC)

When surfactant is continuously added to an amount of water, the surface tension of the water will gradually decrease until it reaches the point where the surface of water is fully packed of surfactant molecule (Hargreaves, 2003). As the concentration of surfactant molecule increase, the extra molecules must be accommodated in the bulk of water, but their low solubility allows for very few of them to exist as an individuals. Most of them are forced to aggregate to form large particles known as micelles. The concentration where aggregation occurs is known as critical micelle concentration (CMC). When the length of lipophilic section of the surfactant chain increase, their water solubility will decrease and leads to a lowering in CMC. Hence, decrease in the solubility of surfactants will decrease the CMC values.

Hait and Moulik (2001) found that the CMC of surfactants can be determined by various methods including tensiometry, conductometry, viscometry, light scattering, fluorimetry, calorimetry, spectrophotometry, and nuclear magnetic resonance (NMR) spectroscopy. Tensiometry, light scattering (turbidity), and spectrophotometry are the most popular techniques used to determine the CMC of the surfactant.

Dominguez *et al.* (1997) identified CMC of some surfactants by UV-Absorption Spectroscopy of benzoylacetone, fluorescence spectroscopy of pyrene monomers and electrical conductivity of an ionic surfactant. They discovered that CMC is found experimentally by plotting a graph of physical character as a function of surfactant concentration. The CMC value is define as the abrupt change of the slope. Nevertheless, the many factors such as temperature and pressure might affect the CMC value. Increase in the hydrocarbon chain-length of a polar group will decrease the CMC value and for ionic surfactants, it also relies on the nature and concentration of counterions in solution. They concluded that the fluorescence method is the most versatile and precise among the three methods since that most of the fluorescence parameters like pyrene are sensitive to the solvent polarity which pyrene is the probe molecule that used to identify the CMC of the micelles.

Other types of CMC determination that commonly used are light scattering (turbidity) method. When micelles form, the turbidity of surfactant solution becomes increased. The water molecules group themselves in a structured way around the hydrophobic part of the surfactant, which may result in decrease in entropy (Edler, 2011). From an energy point of view, the loss in entropy is useful to form aggregate and the surfactant solution become more turbid or cloudy. The smaller particles present in the solution, the lighter beam scatter inside the solution. Properties such as shape and colour of reflectivity of particle inside the solution influence the turbidity and the ability to scatter light through it.

Turbidity can be defined as the concentration of undissolved, suspended particles present in a liquid (Homendra and Devi, 2004). By analyzing the amount of light refracted from the suspended particles in the non-ionic surfactant; the turbidity measurement can be determined.