

Synthesis of Alkyl Polyglycoside Surfactants from Tert-butyl Glycosides and Fatty Acids

Harsa Pawignya^{1,2}, Tutuk Djoko Kusworo¹, Bambang Pramudono¹

¹Department of Chemical Engineering, Faculty of Engineering, Diponegoro University, Semarang 50239, Indonesia, ²Department of Chemical Engineering, University of Pembangunan Nasional "Veteran" Yogyakarta 55283, Indonesia

Abstract

Aim: It is necessary to develop an environmentally friendly type of alkyl polyglycoside (APG) surfactant; this can be done by making surfactants using raw materials based on carbohydrates and fatty acids. The longer the carbon chain in the fatty acid used, the hydrophilic-lipophilic balance will be smaller so it will be easier in choosing the type of surfactant in its use. Until now, there has been no research on the effect of carbon chain length of fatty acids used in the formation of surfactants against surfactant properties. The effect of carbon fatty chain length on surfactant properties can be studied in the following manner. Preparation of APG surfactants was performed with tert-butyl glycoside and various fatty acids (myristic acid, palmitic acid, and oleic acid) using a para-toluene sulfonic acid catalyst. **Results:** Here, there are three reactions, with myristic acid forming tert-butyl miristyl glycoside surfactant (TBMG), with palmitic acid formed tert-butyl palmityl glycoside (TBPG), and with oleic acid to form tert-butyl oleyl glycoside (TBOG). The surfactant was tested for use as an emulsifier in the water-xylene emulsion system, then analyzed the percent emulsion stability and hydrophilic-lipophilic balance (HLB). **Conclusion:** It is found that TBOG is more stable compared to TBPG and TBMG, from HLB values for TBPG and TBOG surfactants are 3.94 and 3.01 so that this surfactant can be used for water-in-oil type emulsifier, for TBMG its HLB value is 11.24 can be used as emulsifier type oil-in-water.

Key words: Chain, myristic, oleic, palmitic, surfactant

INTRODUCTION

Surfactants from petroleum and natural gas derivatives can cause environmental pollution, because after use, it will be a difficult waste to degrade. In addition, the petroleum used is a source of non-renewable raw materials. This is why many people are looking for alternative surfactants that are easily degraded and derived from renewable raw materials. At present, much developed about the synthesis of surfactants with raw materials of carbohydrates, the advantage of using carbohydrate raw materials is biodegradable and non-toxic.^[1] Indonesia is an agricultural country that produces agricultural waste. Agricultural waste contains a lot of carbohydrates composed of cellulose (35–50%), hemicellulose (20–35%), and lignin (10–25%), while cellulose can be hydrolyzed into glucose.^[2]

Alkyl polyglycoside (APG) surfactant is an environmentally friendly nonionic surfactant since it can be synthesized from raw materials

based on carbohydrates and fatty alcohols.^[3] Until now, many APG surfactants have been made which are generally carbohydrate-based raw materials such as glucose and dodecanol (Adisalamun *et al.*, 2012). These surfactants have a carbon chain length of <18, which is less reactive due to the longest carbon chain, the APG surfactant becomes more reactive. APG surfactants are commonly used as additives, substances for emulsion stability in the formulation of some products such as herbicide formulations, personal care products, cosmetics, as well as for the fabrics of fabrics/textiles.^[4]

The surfactant is a molecule having a water-like polar hydrophilic group and a non-polar lipophilic group that likes

Address for correspondence: Bambang Pramudono, Department of Chemical Engineering, Faculty of Engineering, Diponegoro University, Semarang 50239, Indonesia. E-mail: b.purwanggono@undip.ac.id

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oil so that the surfactant can unite a mixture comprising oil and water.^[5] Usefulness of surfactant depends on the value hydrophilic-lipophilic balance (HLB), for examples, HLB value of 1–3 for antifoaming, HLB 2–7 for emulsifier type W/O, HLB 7–9 for wetting, HLB 8–18 for emulsifier type O/W, HLB 13–15 for detergents, and HLB 15–18 for a solvent agent. HLB is a number that indicates the ratio between the hydrophilic and lipophilic groups in a surfactant. The addition of the surfactant in the solution would cause a decrease in surface tension, once it reaches a certain concentration, surface tension will be constant even if the surfactant concentration increased, when the surfactant is added beyond this concentration, the surfactant aggregates to form micelles. The concentration of micelle formation is called critical micelle concentration (CMC).^[6] Various surfactant APG other types made from base ingredients carbohydrates such as surfactants tert-butyl oleyl glycoside (TBOG) and made from the reaction of acetalization of glucose with tert-butanol to produce tert-butyl glycosides (TBG) are then TBG esterified with oleic acid forming surfactant TBOG, TBOG surfactants including APG surfactant group.^[7] Until now, there has been no research on the effect of carbon chain length of fatty acids used in the formation of surfactants against surfactant properties.

In the APG surfactant, generally, the longer the carbon chain in the lipophilic group the HLB value of the surfactant will be smaller so that if used for stabilizing the O/W emulsion system will be better.^[8] The APG surfactant can be used as an emulsifier between oil and water.^[9] The emulsion is the dispersion of a solution (discontinuous phase) in an immiscible liquid (continuous phase). The emulsion is stabilized by the emulsifying agent at the interface between the two liquids, resulting in an electric barrier preventing the unity of the dispersed liquid phase droplets. The demulsification of an emulsion occurs when the electric divider is reduced or removed, causing the breakage of the emulsion.^[10]

The emulsion stability can be maintained by the addition of a third agent called emulsifying agent. The components of the emulsion can be classified into two types: (1) The basic component is the emulsifying agent which must be present in the emulsion. It consists of phase dispersed/phase discontinuous that is liquid divided into small grains into another liquid. The continuation phase is the liquid in the emulsion that serves as the base material (support) of the emulsion. Emulgators are part of an emulsion that serves to stabilize the emulsion. (2) Additional components are an additive that is often added to the emulsion for better results.^[11]

Each emulsifier molecule is divided into two (a) hydrophilic group, the water-like emulsifier member and (b) lipophilic group, the oil-like emulsifier part. Each group will join its preferred liquid, hydrophilic groups in water and lipophilic groups into the oil. Thus, the emulsifier seems to be the binding rope between oil and water with oil, between the two groups will make an equilibrium. Each type of emulgator has a balanced price of equal magnitude. The bigger the HLB

value means, the more water-loving groups, the emulgator is more easily soluble in water and vice versa.^[12]

Based on the particle size, there are three types of emulsions: (1) Macroemulsion, particle size >400 nm (0.4 μm), (2) microemulsion, particle size 10–100 nm (0.01–0.1 μm), and (3) nanoemulsion, particle size 100–400 nm (0.1–0.4 μm). For the type of macroemulsion, there are two most common types of emulsions oil-in-water (O/W) emulsions and water-in-oil emulsions (W/O).^[13] Factors affecting emulsification include the emulsifier type, the temperature, the volume ratio of the two liquid phases, and the properties of the container wall.^[14]

Emulsion stability is a system when droplets retain their initial properties, because the incorporation of droplets is prevented by considerable barrier energy. In general, the energy barrier is built with an emulsifying layer formed on the surface of the droplets (Kjoniksen *et al.*, 2008). Factors affecting emulsion stability include the physical properties of the interface layer; the electrical properties of the droplets; continuous phase viscosity; distribution of droplet size; volume ratio; and temperature (Rosen, 2004; Qiao *et al.*, 2012). A common ingredient used as an emulsion stabilizer is surfactant because the surfactant is almost absorbed irreversibly at the interface. The steric action between the surfactant parts in the dispersing medium is important in this stabilization. The hydrocarbon chain is blocked in its thermal movement if two water droplets close together to close and the hydrophilic head group is dehydrated resulting in close contact. Consequently, hydration repulsion stabilizes the emulsion.^[15]

Emulsion stability refers to the ability of an emulsion to resist the changing properties over time. There are four types of instability in the emulsion: Flocculation, creaming, coalescence, and sedimentation. Flocculation occurs when there is an attraction between the droplets, so they form flocks, such as bunches of grapes. Coalescence occurs when droplets collide with one another and combine to form larger droplets, so the average droplet size increases over time. Emulsions can also experience creaming, where droplets rise to emulsion peaks under the influence of buoyancy, or under the influence of centripetal force induced when centrifuges are used.^[16]

Surfactants can increase the kinetic stability of the emulsion so that the droplet size does not change significantly with time; it is then said to be stable. The use of surfactants for emulsion stability may be performed on oil and water mixtures.^[17] Since agricultural waste is composed of cellulose and cellulose can be hydrolyzed into glucose, the glucose is reacted with tert-butanol to form TBG. In this study, TBG was esterified with various fatty acids having different carbon chain lengths ranging from C_{14} to C_{18} , the fatty acids used were: (1) C_{14} (myristic acid) to form a tert-butyl miristyl glycoside (TBMG) surfactant, (2) C_{16} (palmitic acid) will form tert-butyl palmityl glycoside (TBPG) surfactant, and (3) C_{18} (oleic acid) to form a tert-butyl oleyl glycoside (TBOG) surfactant. From the result of the research, we will

find the relationship between carbon chain length at fatty acid used for esterification, to percent emulsion stability on surfactant stability test, and to other surfactant properties (HLB, CMC, surface tension, yield, and emulsifier type).^[18,19]

MATERIALS AND METHODS

TBGs (49.5%, made from glucose and tert-butanol reactions), oleic acid (merck, 99%), palmitic acid (merck, 99%), myristic acid (merck, 99%), para toluene sulfonic acid (PTSA, merck, 98.5%), xylene $\rho = 0.685$, NaOH (merck, 98%), benzene (merck, 99.7%), and aquades were used.

Surfactant synthesis

Esterification of 0.01 mole TBG with oleic acid (mole ratio 1:4) in 50 ml of benzene solvent and 2% PTSA catalyst with stirring 100 rpm for 4 h at 90°C. The residue was neutralized with NaOH and evaporated until free of water and free of benzene, the result was a TBOG surfactant, then in the same way esterification was repeated, but oleic acid was replaced by using myristic acid, and the result was a TBMG surfactant, then, in the same way, the esterification was repeated using palmitic acid, and the result is a TBPG surfactant. Furthermore, this surfactant performed an emulsion stability test to calculate the percentage of emulsion stability at any given time, surface tension to determine the CMC value (surface tension was measured using tensiometer du nouy), acid number and sapon rate to calculate the HLB value, and the surfactant content analyzed using gas chromatography-mass spectrometry.

Making emulsion

Taken 10 ml of aquades was added Erlenmeyer, then 10 ml xylene, then added TBOG surfactant was varied, then stirred at 10000 rpm for 3 min.

Emulsion stability analysis

The emulsion solution was inserted into the existing volume scale reaction tube, then observed the separate xylene volume at any given time, then calculated percent of the emulsion stability. Determination of emulsion stability in a simple way, by measurement based on separation, assuming that the perfect emulsion system is worth 100 (Bastian *at al.*, 2012).

$$\text{Emulsion stability} = \frac{\text{Xylene volume (Overall-Separation)}}{\text{Xylene volume Overall}} \times 100\%$$

Determination of HLB value

The determination of HLB values can use the following formula (Holmberg *at al.*, 2013).

$$\text{HLB} = 20 \left[1 - \frac{S}{A} \right]$$

Where S = Saponification number, A = Acid number.

RESULTS AND DISCUSSION

Synthesis and surfactant emulsion stability test

In making TBOG surfactant obtained yield 92.20 % and TBOG surfactant content is 91.72 %. Furthermore, an emulsion stability test was performed on the TBOG surfactant. The result of the emulsion stability test on TBOG surfactant can be seen in Figure 1.

Synthesis and TBPG surfactant test

In making TBPG surfactant obtained yield 91.41 % and TBPG surfactant content is 87 %. Furthermore, an emulsion stability test was performed on the TBPG surfactant. The result of the emulsion stability test on TBPG surfactant can be seen in Figure 2.

Synthesis and TBMG surfactant test

In making TBMG surfactant obtained yield 93.12 % and TBMG surfactant content is 89.41 %. Furthermore, an emulsion stability test was performed on the TBMG surfactant. The result of the emulsion stability test on TBMG surfactant can be seen in Figure 3.

From Figures 1-3, it appears that at various surfactant concentrations, the longer the emulsion stability becomes smaller due to the emulsion destabilization process such as cream formation, flocculation, sedimentation, and coalescence (Holmberg *at al.*, 2013).

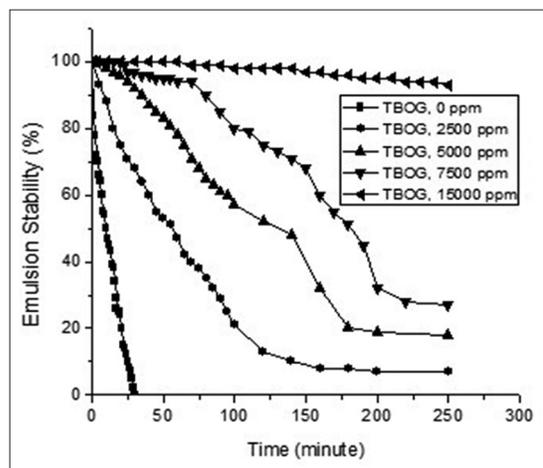


Figure 1: Relationship between percent emulsion stability and time for tert-butyl oleyl glucoside

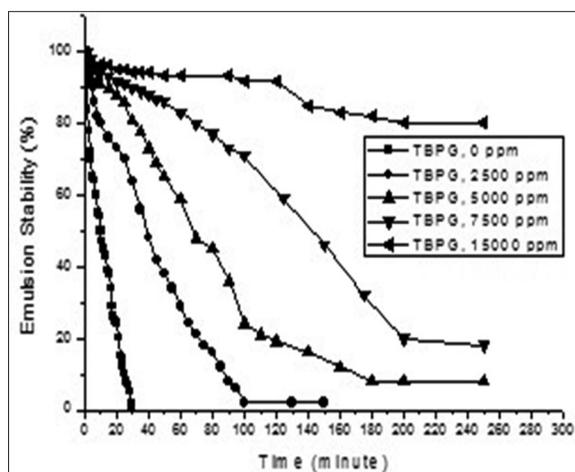


Figure 2: Relationship between percent emulsion stability and time for tert-butyl palmityl glucoside

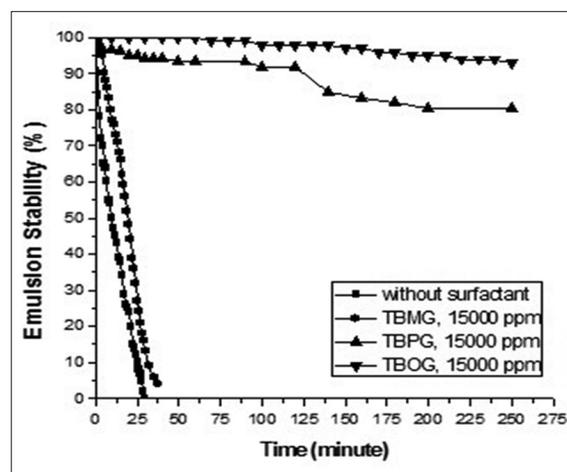


Figure 4: The relationship between percent emulsion stability against time at a concentration of surfactant 15,000 ppm

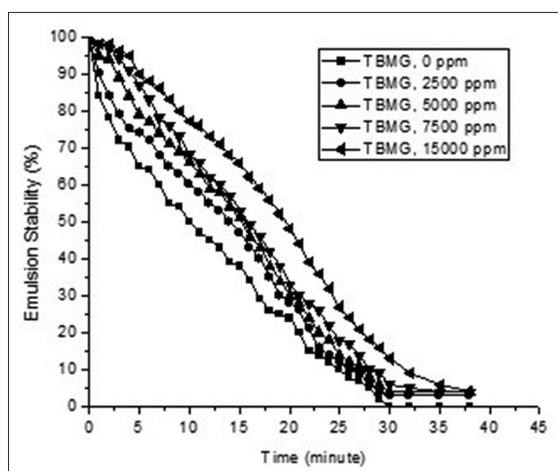


Figure 3: Relationship between percent emulsion stability and time for tert-butyl myristyl glucoside surfactant

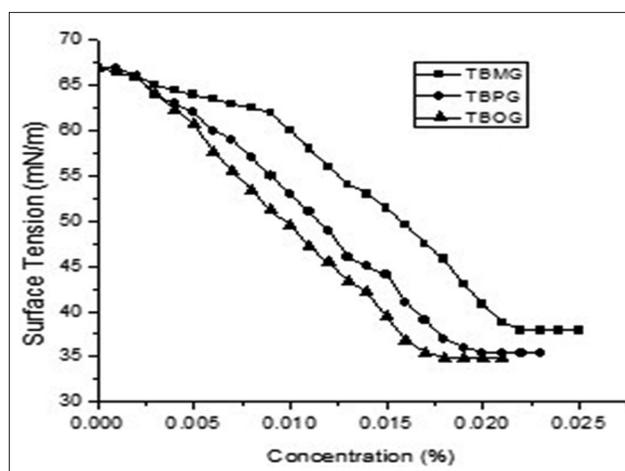


Figure 5: The relationship between surfactant concentrations to surface tension

The greater the surfactant concentration in the emulsion, the higher the emulsion stability, the higher the concentration of the surfactant, and the downward pressure in the emulsion system will be lower so that the emulsion system will be more stable. Figures 1, 2, and 3 show that at a concentration of 15000 ppm surfactant, showing the most stable emulsion system of various surfactants used; this can be illustrated by the following Figure 4.

From Figure 4, it appears that emulsion systems using TBOG and TBPg surfactants are more stable when compared to TBMg surfactants and without surfactants. In Figure 4, it is seen that with time, increasing the percentage of emulsion stability using the TBMg surfactant decreases faster when compared with those using TBOG and TBPg because the TBMg surfactant has the shortest lipophilic group, so the emulsion system is unstable. In the emulsion system without the addition of surfactant, it is seen that with increasing time, then the stability percent of the fastest decreases this because basically xylene cannot mix with water so that although stirred it will quickly separate again.

The stability of the emulsion is influenced by the hydrophilic and lipophilic groups owned by the surfactant. In this test, water is used as a polar material and xylene as a non-polar material, the addition of a surfactant is expected to form an emulsion between water and xylene. The addition of a surfactant may increase the number of hydrophobic groups and lipophilic groups so that the ability to make emulsions between water and xylene increases. In emulsion systems using TBOG surfactants, it is more stable than TBPg and TBMg surfactants. In Figure 3, it is shown that the percentage of emulsion stability using TBMg surfactant is the fastest decrease when compared with those using TBOG and TBPg because the TBMg surfactant has the shortest lipophilic group, so the emulsion system is unstable.^[20]

The stability of the emulsion is influenced by the hydrophilic and hydrophobic groups owned by the surfactant. In this test, water is used as a polar material and xylene as a non-polar material, the addition of a surfactant is expected to form an emulsion between water and xylene. The addition of a surfactant may increase the number of hydrophobic

groups, so the ability to make emulsions between water and xylene increases. The emulsion stability also depends on the length of the hydrocarbon chain on fatty acids used. In general, emulsion stability increases with increasing length of the hydrocarbon chain. This corresponds to steric hindrance arising from the length of the hydrocarbon chain. Emulsion stability measurements need to be done for further applications. Suitable surfactant as an O/W emulsifier is widely used in the industry of self-care products, whereas suitable surfactant as W/O emulsifier is widely used in the food industry (Holmberg *et al.*, 2013).^[21]

Determination of CMC value insurfactant

The result of observation test of various surfactant concentrations to surface tension can be seen in Figure 5.

From Figure 5, it shows that the greater the surfactant concentration in the solution the surface tension inside the solution will decrease to a certain concentration point, then the surface tension will be constant, at that constant point called CMC. This happens because the nature of the surfactant can decrease the surface tension. Figure 5 shows that the value of CMC for surfactant is TBOG = 0.017 % with the lowest surface tension value = 34.4 mN/m, the CMC value of the TBPG surfactant is 0.02% with the lowest surface tension value = 35.4 mN/m and the CMC value of the TBMG surfactant was 0.022 % with the lowest surface tension value = 37.1 mN/m.

Determination of HLB value

From the results of the analysis and the calculation results, the properties of the three surfactants can be seen in Table 1:

Polar molecules tend to be more soluble in polar solvents (water), otherwise non-polar molecules are more soluble

Table 1: Properties of surfactants

Properties	Surfactant		
	TBMG	TBPG	TBOG
CMC, %	0.022	0.020	0.016
S	66.41	68.45	69.56
A	151.61	85.27	81.90
HLB	11.24	3.94	3.01
The lowest surface tension	37.1	35.4	34.4
Yield, %	93.12	91.41	92.20
Content, % V	89.41	87.00	91.72
Type emulsifier	O/W	W/O	W/O

TBMG: Tert-butyl miristyl glycoside, TBPG: Tert-butyl palmityl glycoside, TBOG: Tert-butyl oleyl glycoside, CMC: Critical micelle concentration, HLB: Hydrophilic-lipophilic balance

in non-polar organic solvents (benzene and xylene). Determination of HLB values from all three surfactants (TBMG, TBPG, and TBOG) is required to determine their suitability as emulsifiers. The length of the hydrocarbon chain affects the glucose HLB ester value, the longer the hydrocarbon chain of a glucose ester the lower the HLB value.

Based on Table 1, it can be seen that the TBPG and TBOG surfactants having HLB values of 3.94 and 3.01 so that these surfactants can be used as W/O type emulsifiers. The emulsion with TBOG surfactant is more stable than the emulsion with TBPG. This is due to the length of the TBOG chain longer than the TBPG surfactant whereas for TBMG surfactants having HLB value = 11.24 this can be used as an O/W type emulsifier. The emulsion prepared with the TBMG surfactant is less stable than the emulsion made with the TBPG and TBOG surfactants, thus that the W/O emulsion is more stable than the O/W emulsion W/O emulsion with concentrations >7500 ppm can last longer, while the O/W emulsion can only last for a few minutes.

CONCLUSION

The emulsion stability is proportional to the surfactant concentration; the higher the surfactant concentration is, the higher the emulsion stability will be. The addition of a surfactant may increase the number of hydrophobic groups, so the ability to make emulsions between water and xylene increases. In the emulsion stability test for TBOG surfactant obtained the most stable compared to the TBMG and TBPG surfactants, since the emulsion stability also depends on the length of the hydrocarbon chain of fatty acids used, in general, emulsion stability increases with the increase of hydrocarbon chain length. Length of hydrocarbon chain affects the value of surfactant HLB, the length of the hydrocarbon chain of a glucose ester the lower the HLB value. This is because HLB is a value that depends on the ratio between the hydrophilic and lipophilic chains of a surfactant molecule. The longer the hydrophilic chain is, the higher of HLB value will be. Conversely, the length of lipophilic chain (hydrocarbon) is, the lower of HLB value will be. Surfactant of TBPG and TBOG has HLB values of 3.94 and 3.01 so that this surfactant can be used as an emulsifier of W/O type, whereas for TBMG surfactants having HLB value = 11.24 this can be used as an O/W type emulsifier.^[22,23]

REFERENCES

1. Salamun A, Mangunwidjaja D, Suryani A, Sunarti TC, Arkeman DA. Process optimization for production of alkyl polyglycosides nonionic surfactant using response surface methodology. *J Agroind Technol* 2012;22:51-5.
2. Atta AA, Al-Shafy HI, Mohamed ZM. Application of hydrophobically modified water-soluble polyacrylamide

- conjugated with poly (oxyethylene)-co-poly (oxypropylene) surfactant as emulsifier. *Polym Adv Technol* 2011;22:1879-87.
3. Bangia JK, Om H. Nanoemulsions: A versatile drug delivery tool. *Int J Pharm Sci Res* 2015;6:1363-72.
 4. Bastian F, *et al.* Increased clarity on synthesis process of alkyl polyglycosides (APG) non ionic surfactant based on tapioka and dodecanol. *Reaktor* 2012;14:143-50.
 5. Comelles F, Sánchez-Leal J, González JJ. Soy oil microemulsions made of anionic surfactant, oleic acid, diethyleneglycol ethyl ether and water: Optimized systems. *J Dispers Sci Technol* 2007;28:1218-22.
 6. Corin KC, O'Connor CT. A proposal to use excess Gibbs energy rather than the HLB number as an indicator of the hydrophilic-lipophilic behavior of surfactants. *Miner Eng J* 2014;58:17-21. Corma A, Cambor MA, Iborra S, Miquel S, Primo J, Valencia S. Preparation of environmentally friendly alkyl glucoside surfactants using zeolites as catalysts. *J Catal* 1996;161:713-9.
 7. El-Sukkary MM, Nagla A, Aiad SI, El-Azab IM. Synthesis and characterization of some alkyl polyglycosides surfactants. *J Surfact Deterg* 2008;11:129-37.
 8. Hait SK, Moulik SP. Determination of critical micelle concentration (CMC) of nonionic surfactants by donor-acceptor interaction with iodine and correlation of CMC with hydrophile-lipophile balance and other parameters of the surfactants. *J Surfact Deterg* 2001;4:303-9.
 9. Hill H, Rhode O. Sugar-based surfactants for consumer products and technical applications. *Fett Lipid* 1999;101:25-33.
 10. Holmberg KJ, Lindman B, Kronberg B, Jönsson B. *Surfactants and Polymers in Aqueous Solution*. 2nd ed. Chichester, New York: J Wiley; 2013. p. 451-71.
 11. Kjøniksen AL, Kotlar HK, Beheshti N, Nyström B. Modified Polysaccharides for use in enhanced oil recovery applications. *Eur Polym J* 2008;44:959-67.
 12. Li C, Mei Z, Liu Q, Wang J, Xu J, Sun D. Fermentation and properties of paraffin wax submicron emulsions prepared by the emulsion inversion point method. *Colloids Surf A Physicochem Eng Aspects* 2010;356:71-7.
 13. Mattei M, Kontogeorgis GM, Gani R. Modeling of the critical micelle concentration (CMC) of nonionic surfactants with an extended group-contribution method. *Ind Eng Chem Res* 2013;52:12236-46.
 14. Nesterenko A, *et al.* Influence of a mixed particle/surfactant emulsifier system on water-in-oil emulsion stability. *Colloids Surf A Physicochem Eng Aspects* 2014;457:49-57.
 15. Pawignya H, *et al.* Synthesis tert-butyl oleyl glycosides surfactant from esterification tert-butyl glycosides with oleic acids. *Adv Sci Lett* 2017;23:5716-9.
 16. Qiao W, Li J, Zhu Y, Cai H. Interfacial tension behavior of double long-chain 1, 3, 5-triazine surfactants for enhanced oil recovery. *Fuel* 2012;96:220-225.
 17. Raikar NB, Bhatia SR, Malone MF, McClements DJ, Almeida-Rivera C, Bongers P, *et al.* Prediction of emulsion drop size distributions with population balance equation models of multiple drop breakage. *Colloids Surf A Physicochem Eng Aspects* 2010;361:96-108.
 18. Rosen MJ. *Surfactants and Interfacial Phenomena*. 3rd ed. New Jersey: John Wiley and Son; 2004. p. 303-20.
 19. Saha BC. *Lignocellulose Biodegradation and Application in Biotechnology*. US Government Work: American Chemical Society; 2004. p. 2-14.
 20. Ware AM, Waghmare TJ, Momin SA. Alkyl polyglycoside: Carbohydrate based surfactant. *J Dispers Sci Technol* 2007;28:437-44.
 21. Xu F, Riemer N, Wang DP. Modeling flocculation processes of time-grained particles using a size resolved method: Comparison with published laboratory experiments. *Con Shelf Res* 2008;28:2668-77.
 22. Xu J, Yin A, Zhao J, Li D, Hou W. Surfactant-free microemulsion composed of oleic acid, n-propanol, and H₂O. *J Phys Chem* 2013;117:450-6.

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