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Synthesis of Surfactant Tert-Butyl Glycosides from Glucose and Tert-Butanol

Harsa Pawignya [1,2], Tutuk Djoko Kusworo[1] and Bambang Pramudono[1*]

[1]Department of Chemical Engineering, Faculty of Engineering, Diponegoro University
Jl. Prof. Soedarto, SH, Tembalang, Semarang
[2]Department of Chemical Engineering, Faculty of Industrial Engineering, University of Pembangunan Nasional "Veteran" Yogyakarta, Jl. SWK 104 Condongcatur Yogyakarta

*) Corresponding author: harsa_paw@yahoo.co.id

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Abstract

In Indonesia, a lot of discarded agricultural waste still contains cellulose (35-50%), the waste can still be hydrolyzed to glucose and then used as raw material in the manufacture of surfactants. Glucose can be reacted with tert-butanol using a para-toluene sulfonic acid catalyst to form tert-butyl glycoside surfactant. The purpose of this study was to study the process conditions influence the variable mole ratio, temperature, and catalyst percent on the yield of tert-butyl glycosides. The results showed that at mole ratio 1:5; temperature 70^{o}C; and the percentage of catalyst 2.5 %, the yield obtained was 98.58 % with tert-butyl glycosides content of 61.2 %. Furthermore, the molecular structure of the surfactant was analyzed using FTIR while surface tension to determine the hydrophilic-lipophilic balance (HLB) value and obtained an HLB value of 4.61 Therefore, tert-butyl glycoside surfactant can be used as an emulsifier in the water-in-oil emulsion system.

Keywords: *glucose; surfactant; tert-butanol; tert-butyl glycosides*

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INTRODUCTION

Developed countries in general, renewable products are accepted under some conditions that the product does not damage the environment, not raw material, and neither polluting the environment when in its production process. Meanwhile, the need for surfactant has been increasing along with the increase of industrial development (Adisalamun, *et al*, 2012). Surfactant of petroleum and gas can pollute the environment, for after being used, it will turn into highly non-degradable waste. For this reason, alternatives for readily degradable surfactant have been explored (El-Sukkary, *et al*, 2008). 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 (Saha, 2004).

In this past 10 years, a lot of research regarding the production of surfactant out of carbohydrate has been widely carried out. This is because surfactant

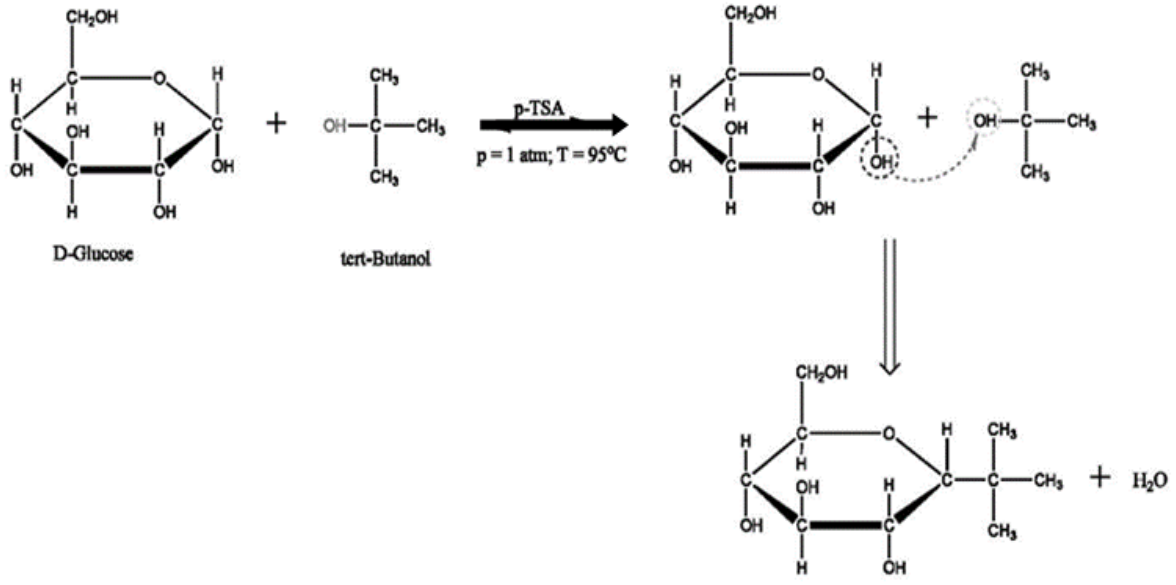
with carbohydrate as its raw material is biodegradable and non-toxic (Corma, *et al*, 1996). Carbohydrates are growing important renewable raw material for surfactant industry. The development of surfactants based on carbohydrate and vegetable oils is the result of the product concept based on the exclusive use of natural resources. Sugar based surfactants are gaining increased attention due to advantage with regard to performance, health of consumer and environmental compatibility compared to some standard product. Alkylpolyglycoside (APG) is nonionic surfactant prepared from renewable raw materials, namely glucose and fatty alcohol. Such products are expected to exhibit surface-active properties due to the presence of the hydrophilic sugar moiety and the hydrophobic fatty alcohol residues (Ware, *et al,* 2007).

Surfactant is a surface-active agent acting to help reduce the surface tension. The action of surfactant is triggered by the multiple characteristics of its molecule, which is composed of hydrophilic and lipophilic groups. The hydrophilic part is polar, a condition that can be electrically positive charged (cationic surfactant), negative (anionic surfactant), neutral (non-ionic surfactant); as for the lipophilic part, it is alkyl (Qiao, *et al,* 2012; Xu, *et al*, 2013).

These two groups carry hydrophilic and lipophillic balance, which then helps indicate whether the surfactant is emulsified, wetting, solvent, detergent or anti-foam, and so on (Nesterenko, *et al,* 2014; Mattei, *et al,* 2014). Kirk (1998) has carried out an asetalization reaction of glucose and chloropropane, in which asetalization occurs in the position of C_1 hydroxyl groups hemiacetal with the group of hydroxyls of propanol. Surfactant of tert-butyl galactocidase through an asetalization reaction of galactose and tert-butanol has been synthesized using p-TSA catalyst and the result indicates a CMC of 0.02 % and hydrophilic-lipophilic balance (HLB) of 3.93 (Sembiring, 2007). The application of surfactant would normally be based on the value of HLB of the surfactant; the higher the HLB, more soluble in water the surfactant is; and conversely, the lower the HLB, the more soluble in oil it is (Corin and O'Connor, 2014; Kjøniksen, *et al*, 2008; Atta, *et al*, 2011).

Usefulness of surfactant depends on the value HLB, for examples of 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 a surfactant was added beyond this concentration, the surfactant aggregates to form micelles. The concentration of micelle formation called the Critical Micelle Concentration (CMC) (Rosen, 2004).

This encourages the need to synthesize a new type of APG surfactant that uses environmentally friendly raw materials namely tert-butyl glycoside (TBG), from the reaction of glucose with tert-butanol using a p-TSA catalyst. The goal is to find the operating conditions (mole ratio, temperature and percent catalyst) that can produce the maximum TBG yield, determine the reaction kinetics value and determine the molecular structure of TBG. Specific properties of TBG surfactants are can be used as emulsifiers for water in oil emulsion systems. The reaction produces a target compound of tert-butyl glycoside that carries groups of ether, hydroxyl, and alkyl, and they have the characteristics of a surfactant (Comelles, *et al*, 2007).



(1)

This reaction is equivalent to the following reaction:

$A + B \rightarrow C + D$ (2)

$$-\frac{d\,C_A}{dt} = k\,C_A C_B \quad (3)$$

The mole ratio (mole tert-butanol/mole glucose) is made larger, so that the reaction follows a pseudo-order reaction (Carraher, *et al*, 2015).

$$-\frac{d\,C_A}{dt} = k'\,C_A \quad (4)$$

$k' = k\,C_B$, a pseudo order reaction (5)

$$\ln C_A - \ln C_{A0} = -k'\,(t-0) \quad (6)$$

$$\ln C_A = \ln C_{A0} - k'\,t \quad (7)$$

$$k' = \frac{\ln C_{A0} - \ln C_A}{t} \quad (8)$$

MATERIALS AND METHODS

Materials

Glucose (Merck, 99 %), tert-butanol (Merck, 98 %), petroleum ether (Technical), para toluene sulfonic acid (p-TSA) (Merck, 98.5 %), cupric sulfate (Merck, 99.28 %), natrium sulfate (Merck, 98 %), aquadest.

Methods

As much as 9 g (0.05 gmole) of glucose and tert-butanol (with mole ratio variation) was put into a 500 ml three-necked flask equipped with a mixer, a thermometer, a heater, and a chiller (its function is to cool the steam to condense). It was then added to 50 ml of petroleum ether and p-TSA catalyst (the percent of the catalyst varied) and was then mixed and stirred for 2 hours under varied temperatures. And then, it was refluxed until no water was left from the distillation. The water was contained in a separatory funnel after being tested using cupric sulfate. The result of the reaction was cooled down in a room temperature to be then added with 0.2 g anhydrous Natrium sulfate and stirred. After that, it was screened, and the resulted filtrate was evaporated. The residue was weighed and evaporated and reweighed again until constant weight was obtained. The result left was the tert-butyl glycosides. Finally, the yield, CMC value, and HLB value were calculated. CMC value obtained from the graph the relationship between surface tension with TBG concentration, CMC value selected at the smallest concentration to achieve surface tension constant value. Then the HLB value can be calculated by Equation (9).

$$HLB = 7 - 0.36\ln\frac{100 - CMC}{CMC} \quad (9)$$

Analytical tools: Molecular groups using Fourier Transform Infrared Spectrophotometer (FTIR, 640-IR, California) (Ashokkumar and Ramaswamy, 2014), analysis of surface tension using Du Nuoy ring method surface Tensiometer (JZHY-180, China), glucose and TBG analyzed using volumetric analysis.

RESULTS AND DISCUSSION

The results of research, the effect of the variable mole ratio, temperature and percent of catalyst is as follows:

Effect of mole ratio into yield

Reaction is carried out on 1.5 % catalyst, stirring speed 100 rpm, reaction time 2 hours and temperature 65 °C. Data of effect of mole ratio variable to yield can be seen in Figure 1.

Figure 1. indicates that the more mole ratio is used, that is, from 2 to 5, the higher yield is obtained. This is because when a reactant is excessively made, the reaction will move to the right and that will make the yield bigger, but after the mol ratio of 1: 5, the yield is close to constant. This is because the more tert-butanol can cause the pH to go down from 6.3 to 5.8 so that the glucose bonds with tert-butanol can be released again. Bonds can be released again if it is acidic (Prito-Arias, *et al*, 2007).

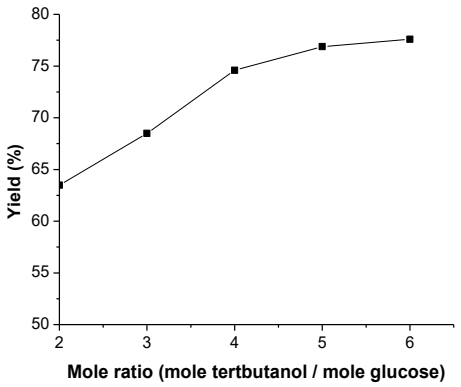


Figure 1**.** Effect of mole ratio into Yield

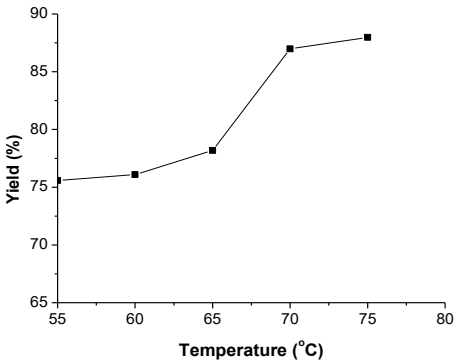


Figure 2. Effect of Temperature into Yield

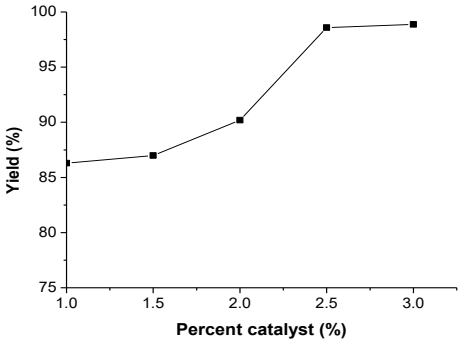


Figure 3. Effect of Percent Catalyst p-TSA into Yield

Effect of temperature into yield

Reaction is carried out on 1: 5 mole ratio, 1.5 % catalyst, 100 rpm stirring rate, 2 hours reaction time and temperature value varies. Data of influence of variation of temperature to yield can be seen in Figure 2.

Figure 2. indicates that starting from 55 ^{o}C up to 70 ^{o}C the value of yield obtained is getting bigger. This occurs because with increasing temperature the reaction speed to the right will be faster, so products are increased, and the yield will be greater. However, after 70 ^{o}C, the yield that is near constant is obtained. This is because above 70 ^{o}C, the bond between glucose and tert-butanol is released again. Bonds can be released again if they are acidic and heat (Prito-Arias, *et al*, 2007).

Effect of amount of catalyst p-TSA on yield

Reaction is carried out on 1: 5 mole ratio, percent of catalyst was varied, stirring speed 100 rpm, reaction time 2 hours and temperature 70 ^{o}C. Data of effect of percent catalyst variable on yield can be seen in Figure 3.

Figure 3. indicates that 1 % to 2.5 % of catalyst will result in higher yield. This is because when the more percent of catalyst is provided, the less the activation energy is required, consequently the reaction speed is getting faster, and the yield is also getting bigger. However, when more than 2.5 % of catalyst is used, yields are getting smaller and closer to constant. This is because the more p-TSA catalyst causes the pH value to be smaller from 6.3 to 5.7 so that the bond between glucose and tert-butanol will be released again. Bonds can be released again if it is acidic (Prito-Arias, *et al*, 2007).

Best condition

The best condition was reached when the mole ratio was 1:5, temperature 70 ^{o}C and the percent of catalyst was 2.5 %. This condition produced as much as 98.58 % of yield, TBG content of 61.20 %. Under these conditions with C_{A0} = 0.05 gmole, C_A = 0.0265 gmole and time 120 minutes, then from Equation (8) obtained value k' = 0.00529/minute. Then the TBG produced under this condition is subjected to analysis of the structure of the molecular group using FTIR. Next to determine the HLB and CMC values, a surfactant solution with various concentrations was made and then the solution was analyzed for surface tension values, the results can be seen in Figure 6.

Structure Groups analysis using the FTIR method

FTIR analysis is used to identify the functional groups of glucose as reactants and products TBG, the results can be seen in Figure 4 and 5.

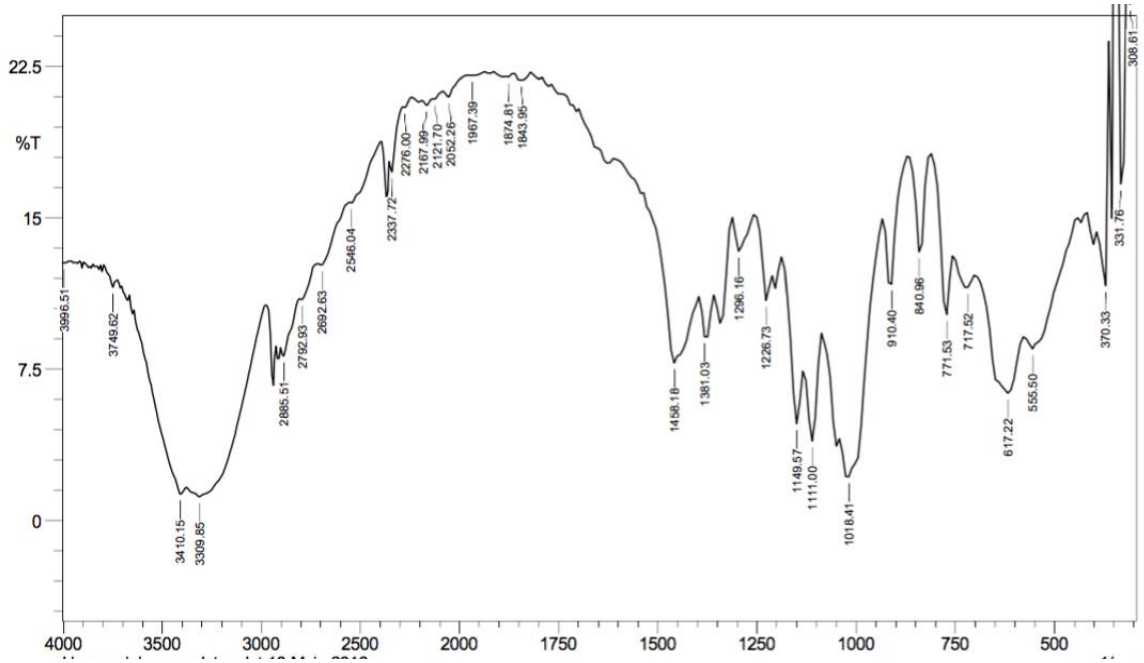


Figure 4**.** Relationship between wave number and percents of transmission of FTIR Glucose

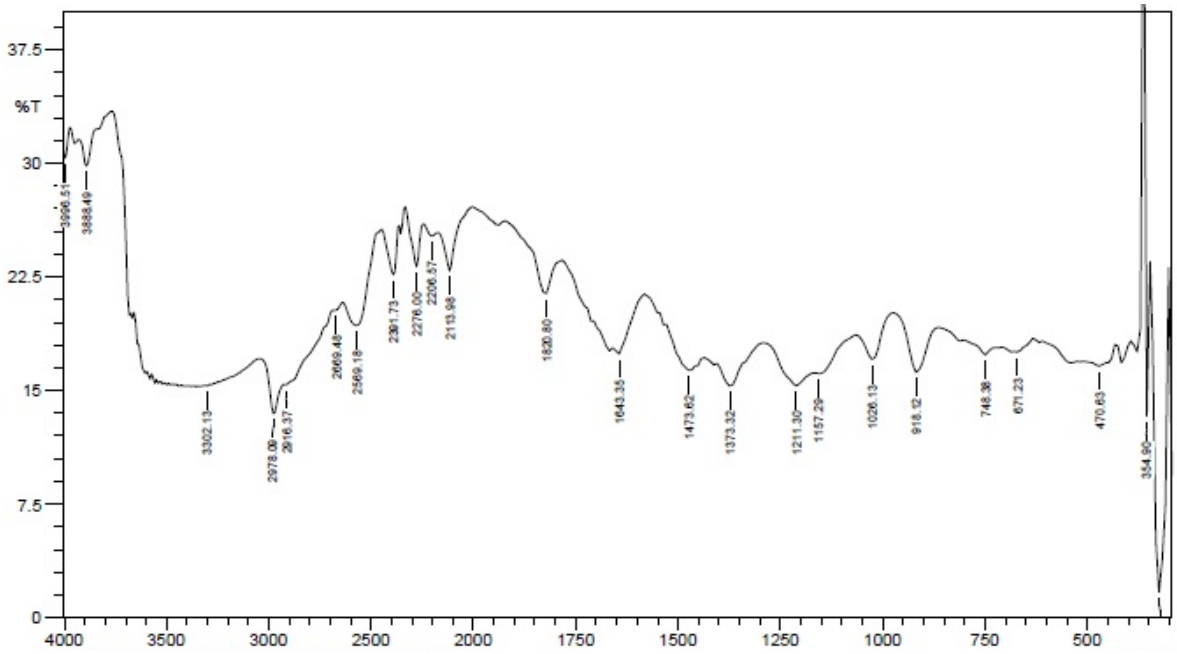


Figure 5**.** Relationship between wave number and percents of transmission of FTIR TBG

Table 1. Interpretation of FTIR analysis of glucose and tert-butyl glycosides

Structure groups	Waves number (cm^{-1})		
	Range El-Sukkary	Gyucose	Tert-butyl glycosides
O-H	2978 – 3371	3309	3302
C-O-C	1072 – 1165	1149	1157
CH_2	702 – 749	717	748
CH_3	2924 - 3032	-	2978
C-O	979 - 1064	1018	1026

Figures 4 and 5. show the correlation between wave number and percents of transmission for glucose molecules and TBG molecules. The peak analysis is provided in Table 1.

Table 1. shows in the glucose molecule there are O-H groups, C-O-C groups, CH_2 groups, and C-O groups and shows that the wave number within the tert-butyl glycoside molecule carries O-H groups, C-O-C groups, CH_2 groups, CH_3 groups and C-O groups, so there is a difference with a glucose molecule. This fact clearly indicates that there is tert-butyl glycoside produced in the reaction.

Determining the Values of CMC and HLB tert-Butyl Glycoside

Solution of tert-butyl glycoside in water with various concentrations were made, and it then analyzed for the value of surface tension using the Du Nuoy Tensiometer as the result shown in Figure 6. Figure 6. indicates that in the beginning the concentration of TBG is increasing and the surface tension is decreasing and becoming constant even when the amount of the concentration is increased (Guilbot, *at al*, 2013). This is because the addition of tert-butyl glycoside surfactant in the solution will cause a decrease in surface tension. After reaching a certain concentration, the surface tension will be constant, this is because the concentration becomes saturated and the micelle is formed. This condition is called Critical Micelle Concentration (CMC).

Figure 6. tells us that the CMC value of the tert-butyl glycoside, is 0.13 %, the level of which can reduce the surface tension of as low as 42.35 mN/m. As for the water surface tension of 67.5 mN/m at the temperature of 30 ºC. Of the CMC value, there can be obtained the HLB value of about 4.61. This shows that the results are different from the results of previous studies, ie with galactose and tert-butanol materials having a tert-butyl galactocidase surfactant having CMC value = 0.02% and HLB value = 3.93 (Sembiring, 2007).

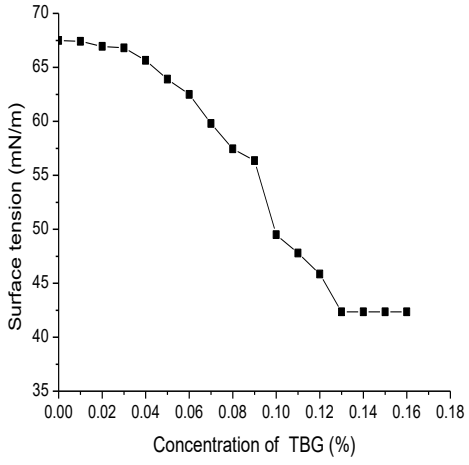


Figure 6. Relationship between Concentration of TBG and Surface Tension

The decrease of the surface tension is triggered by the interactions between water molecules and tert-butyl glycoside the latter of which carries hydrophilic groups (C-O-C, CH_3, O-H) and lipophillic groups (CH_2 and C-O) to help build micelles (Kirk, et al, 1998). Table 1. and Figure 6. shows that the molecular group structure of glucose differs from TBG, in TBG there is group CH_3 so that in TBG solution can decrease the surface tension to CMC point. It can be said that TBG can be used as an emulsifier, while glucose cannot be used as an emulsifier.

This interaction weakens the bonds between of hydrogen and water molecules on the surface. The HLB value indicates that the tert-butyl glycoside, is one of the non-ionic surfactants that can serve as emulsifiers type water in oil (HLB value of 2 - 7), (Rosen, 2004)

CONCLUSIONS

For the synthesis of surfactant tert-butyl glycosides of asetalization reaction of glucose with the tert-butanol obtained the best conditions are the mole ratio is 1:5, the temperature is 70 ^oC, the percent of catalyst is 2.5 %; and the yield is 98.58 %, value k' = 0.00529/minute. The FTIR analysis indicates that with various wave numbers of tert-butyl glycoside molecules already produced, there are found three groups of O-H, C-O-C, CH_3, and C-O. From the analysis obtained the content of TBG 61.2 %. This finding confirms that the reaction helps form tert-butyl glycoside. It was also found out that the tert-butyl glycoside surfactant obtained carries the value of CMC 0.13 % and value of HLB 4.61. Confirm that this surfactant belongs to the type of water-in-oil emulsifier (W/O).

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