

Surface and Dispersion Properties of Dodecanol and Tetradecanol Based Glucoside Surfactants

Geetha D¹, Rashmi Tyagi¹

Abstract— The sugar based alkyl polyglucosides have been synthesized from fatty alcohols and dextrose on laboratory scale to find the optimum molar ratio of the paratoluene sulfonic acid catalyst for the synthesis in lower reaction temperature and pressure. The chemical structures and purity of the synthesized compounds were confirmed by using fourier transform infrared spectroscopy and nuclear magnetic resonance spectroscopy. The surface and interfacial properties like critical micelle concentration, free energy of micellization, surface excess concentration and surface area demand per molecule were determined. These sugar based surfactants have been found to exhibit good surface tension, emulsion stability, foaming and wetting power. A new approach through nephelometric measurements has been followed to measure the dispersion power and the synergy with sodium dodecylglucosides. A good amount of synergism was found between the alkyl polyglucosides and the anionic sodium dodecyl surfactant. Biodegradation studies showed that the primary biodegradability of the synthesized surfactants was above 80%.

Index Terms— Biodegradability, Dispersion, Dodecyl glucoside, Emulsion stability, Foaming ability, Synergism, Tetradecyl glucoside, Wetting.

1 INTRODUCTION

The concern about the environment for the sustainable growth, enhance the development of biodegradable, non-toxic and naturally derived surfactants. In this regard, sugar based alkyl polyglucosides have been growing as a new class of nonionic surfactant with their good environmental profile [1] mild character [2] dermatological compatibility and novel surface active properties [3], [4], [5]. The naturally abundant, multifunctional sugar moiety constitute the hydrophilic part increase the chance for new derivatized APG surfactants with desired properties. The optimum molar ratio of the PTSA (Para toluene sulfonic acid) catalyst have been analyzed in the present study for the synthesis of alkyl polyglucosides by the condensation reaction of anhydrous glucose and fatty alcohols of different alkyl chain length (C_{12} & C_{14}). The prepared compounds have been evaluated as potential surfactants and to assess the improvement in the physicochemical properties of the APG surfactants and in turn to expand their potential applications.

2 EXPERIMENTAL TECHNIQUES

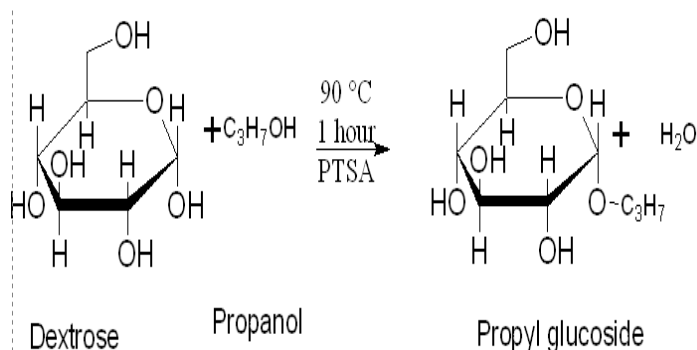
2.1 MATERIALS AND METHODS

All the chemicals used throughout this study were used as such without any further purification. D-Glucose, sodium dodecyl sulfate (SDS) and fatty alcohols were supplied by Merck, p- toluene sulfonic acid (PTSA) was supplied by Loba Chemical Company. Double distilled water was used for preparing solutions.

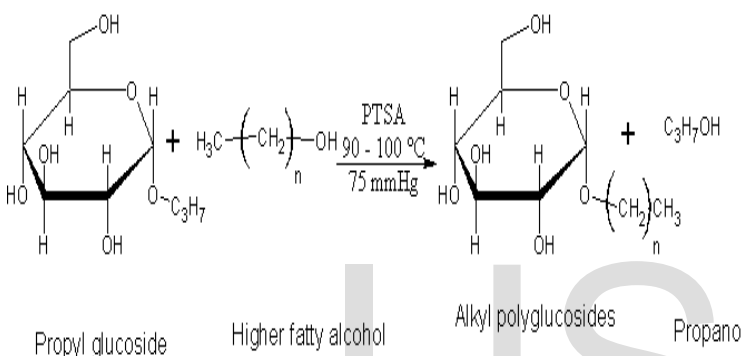
2.2 Preparation of APGs

Since the synthesis of APGs of varying chain length have been reported already, the present study deals with the role of PTSA catalyst in synthesis of APG₁₂ and APG₁₄ by the condensation reaction of glucose and fatty alcohol of different alkyl chain length (C_{12} & C_{14}) using varying molar ratio of acid catalyst PTSA [6]. It is a two step process as represented in Scheme - 1. In the initial step, a measure of 5.4g of anhydrous dextrose was dissolved in 18g of propanol in the presence of 0.4g PTSA with azeotropic removal of water at 90°C for 1 hr. Then 27.95g (dodecanol) and 32.15g (tetradecanol) of the higher alcohol and 0.06 - 0.095g of PTSA was added slowly with increasing temperature to 90°C - 100°C under vacuum (75 mm Hg), until completion of the reaction. The reaction was quenched by adding 1% alcoholic NaOH and the mixture was stirred for additional 30 min. The residual alcohol was removed by multistage vacuum distillation at 80°C. Step- I Synthesis of propyl glucoside intermediate

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Step-I Synthesis of propylglucosides.



where $n = 11$ for Dodecyl glucoside, 13 for Tetradecyl glucoside.

Step-II Transacetalization by higher alcohols to alkyl polyglucosides.

Scheme 1 Synthetic route of alkyl polyglucoside.

2.3 Molecular Structure Confirmation of APGs

The structure of the final product was confirmed using, FTIR model Thermo Nicolet, Avatar 370, ¹H-NMR model Bruker Avance III, 400 MHz, and ¹³C - NMR model Bruker Avance III, 100 MHz. All these spectral analysis were performed at Sophisticated Analytical Instrument Facility (SAIF), Cochin, Kerala, India.

2.4 SURFACE/INTERFACIAL ACTIVE PROPERTY OF THE ALKYL POLYGLUCOSIDES

The surface property of the synthesized APGs have been analyzed primarily by surface tension measurements using Du-Nouy ring tensiometer at different temperatures and concentrations. The surface tension of APG₁₂ was determined

at three different temperatures viz. 25°C, 45°C and 55°C where as for APG₁₄ it was determined only at 45°C and 55°C as APG₁₄ is not soluble at 25°C in water. The other surface properties were calculated from the following formulae [7].

$$\text{Surface excess concentration: } \Gamma = - (1/iRT) (d\gamma/d\ln C) \quad - (1)$$

Specific surface area:

$$A_{CMC} = 1/N \Gamma_{CMC} \quad - (2)$$

Free energy of micellization:

$$\Delta G_{CMC} = 2.303RT \log C_{CMC} \quad - (3)$$

Where, γ - surface tension (mNm⁻¹), R - gas constant (8.314Jmol⁻¹ K⁻¹), T - Absolute temperature, C - Surfactant concentration, $(d\gamma/d\ln C)$ - Slope of surface tension plots, N - Avagadro's number (6.022×10^{23}), G - Free energy
The value of i represent the number of species at the interface for which the concentration changes with the surfactant concentration. The co-efficient $i = 1$ for the dilute solution (10^{-2} M or less) of synthesized alkyl polyglucosides [8].

2.5 BIODEGRADABILITY

The biodegradability of aqueous solutions of APGs was conducted according to the OECD 301 E test for ready biodegradability [9] and the APGs were quantified by a modification of the anthrone method proposed by Buschman and Wodarczak [10]. The biodegradation were tested by taking 1.2 litres (15mgL⁻¹) of APGs aqueous solution with nutrients in a 2 litre Erlenmeyer flask and inoculated with active sludge of sewage treatment plant. The residual APG concentration over time was determined by mixing 2ml of degradation liquor with 5ml of solution of 0.8% (w/w) anthrone in conc. H₂SO₄. The mixture was hydrolysed for 5 min in boiling water and then quickly cooled in cold water for 10 minutes. The absorbance of this mixture was studied at 621nm by using single beam UV-visible spectrophotometer [11]. In order to know the biodegradability of APGs in an ordinary condition, the aqueous APG surfactant in the same concentration was made with sewage water. The residual surfactant concentration have been measured with anthrone reagent at different time intervals.

2.6 DISPERSING POWER OF APGS

The dispersing power of the synthesized APGs for decanol have been analyzed by using digital nephelometry meter

(model No. CL 810). The synergism of the synthesized APGs with the anionic SDS in term of turbidity have been analyzed by using nephelometer. The polar oily material decanol in different quantities have been mixed to the aqueous solution of 0.01M APGs (APG₁₂ and APG₁₄ respectively), 0.01M SDS and their mixtures of various molar ratios viz 4:1, 3:2, 2:3 and 1:4. The dispersed decanol in the surfactant was allowed to attain equilibrium by stirring them in a thermostat for 5 hr at 30°C. The dispersion caused the turbidity. The turbidity of mixtures of aqueous surfactant solution and decanol was measured using digital nephelometry meter (model No. CL 810). This test was designed to be simple and to provide a relative comparison of the dispersion and solubilization of decanol in the mixtures of APG₁₂ + SDS and APG₁₄ + SDS to prove their synergistic nature.

2.7 PERFORMANCE PROPERTIES

The following performance properties were evaluated with the 0.1 % aqueous APGs surfactant solutions.

2.7.1 FOAMING

The foaming power of 0.1% (20ml) solution was determined by pouring the surfactants into 100 ml stoppered measuring cylinder and whipping with a perforated plunger, giving 30 constant vigorous strokes by hand. The volume of the foam produced was read immediately and after 5 min [12].

2.7.2 EMULSION STABILITY

Emulsion stability determination was done from 10 ml of 0.1% aqueous solution of the APGs with 10 ml of light paraffin oil and shaken vigorously for 2 min at 25°C. The emulsifying power was determined by the time it took for the clear aqueous volume separating from the emulsion layer to reach 9 ml, counting from the moment the shaking was stopped [6],[13].

2.7.3 WETTING

Wetting time was determined by immersing a sample of cotton fabric (4cm×4cm) in 20ml of 0.1% aqueous solution of APGs at 25°C. The time was recorded from the moment, the cotton fabric was put into the solution until the moment it started going down and settle down on bottom [14].

3 RESULTS AND DISCUSSION

3.1 EFFECT OF CHANGE OF MOLAR QUANTITY OF PTSA ON YIELD OF APGs

The yield of synthesized alkyl polyglucosides are reported in Table 1. On perusal of table 1, it can be revealed that catalyst PTSA is playing an important role on the final yield of APGs like controlling the polyglucoside side product formation, and improving quality of the final APG products. Three different batches have been carried out, viz 0.004 mole PTSA, 0.005,

0.006. When the amount of acid catalyst increased, the product yield have also been increased. Beyond the optimum molar ratio (0.005), the catalyst increased the unwanted polymerization of the polyglucose side product and there was a decrease in the formation of desired glucoside product. Maximum yield of APGs were observed when molar quantity of PTSA was 0.005. In the case of APG₁₂ the yield was 38.0%, for APG₁₄, it was 37%. When the molar ratio of PTSA was increased to 0.006 moles then, instead of rise of the yield, there was a decrease in the yield, for APG₁₂, it was 36.5 and for APG₁₄, it was 35.7%.

Table 1 Effect of varying molar ratios of PTSA on yield of APGs (C₁₂ & C₁₄).

S. N o.	APG ₁₂		APG ₁₄	
	Molar ratios	Yield of APG ₁₂ (%)	Molar ratios	Yield of APG ₁₄ (%)
	Glucose : Dodecanol : PTSA		Glucose : Tetradecanol : PTSA	
1	01 : 05 : 0.003	36.0	01 : 05 : 0.003	35.0
2	01 : 05 : 0.005	38.0	01 : 05 : 0.005	37.0
3	01 : 05 : 0.006	36.5	01 : 05 : 0.006	35.7

3.2 STRUCTURE CONFIRMATION

FTIR SPECTROSCOPY: The molecular structure of the synthesized APG₁₂ and APG₁₄ was confirmed using FTIR spectroscopy.

A typical FTIR spectrum of APG₁₂ displayed bands at 3100–3300 cm⁻¹ (O-H), 1050 cm⁻¹ (C-O), 1726 cm⁻¹ (CHO), 1117 cm⁻¹ (C-O-C), 2855 cm⁻¹ (CH₃-symmetric stretch), 2922 cm⁻¹ (CH₃-asymmetric stretch), 1645 cm⁻¹ (CH₃- asymmetric bending), 1371 cm⁻¹ (CH₃-symmetric bending), 1459 (CH₂-asymmetric bending), 720 cm⁻¹ (multiple (CH₂)_n rock) which are characteristic of the desired compound.

The Synthesized APG₁₄ displayed bands at 718 cm⁻¹ (multiple (CH₂)_n rock), 1464 cm⁻¹ (CH₂ asymmetric bending), 2852 cm⁻¹ (CH₂ symmetric bending), 3200 – 3400 cm⁻¹ (O-H), 1057 cm⁻¹ (C-O), 1715 cm⁻¹ (CHO), 1127 cm⁻¹ (C-O-C), 2855 cm⁻¹ (CH₃-symmetric stretch), 2865 cm⁻¹ (CH₃-asymmetric stretch), 1463 cm⁻¹ (CH₃- asymmetric bending), 1376 cm⁻¹ (CH₃-symmetric bending) which are characteristic of the desired compound.

¹H-NMR spectra: The synthesized APG surfactants were further supported by the ¹H-NMR spectrum which exhibits signals for APG₁₂. Δ 0.85 (t, 3H, CH₃), 1.23 (20H, CH₃ (CH₂)₁₀), 3.47 (2H, O-CH₂ (CH₂)₁₀), 3.44-4.6 (m, glucoside protons).

APG₁₄. Δ 0.86 (3H, CH₃), 1.25 (26H, CH₃ (CH₂)₁₃), 3.37 (2H, O-CH₂(CH₂)₁₄), 3.04-4.26 (m, glucoside protons).

The ¹³C-NMR was performed to confirm the type and distribution of carbon atoms in the prepared surfactants.

3.3 SURFACE/INTERFACIAL ACTIVE PROPERTIES OF THE ALKYL POLYGLUCOSIDE SURFACTANTS

3.3.1 SURFACE TENSION

The surface tension values were measured are depicted in Figure 1, 2. In the beginning, with the increase of surfactant

concentration, the surface tension values got decreased up to the CMC; above the CMC, the surface tension values were not decreased.

The surface tension values decreased with the increase of temperature for the same concentration of APGs than that of the higher concentration due to the loss of heat energy happened when the hydrogen bond between the free hydroxyl groups of APGs with water get break down. The loss of heat energy was higher at higher concentration than that at the lower concentrations.

For the constant hydrophilic glucose moiety, the effect of length of hydrophobic group has been studied. The surface tension values decreased with increase of alkyl chain length. The solubility of the surfactant decreased on the increase in the alkyl chain length due to the increase of hydrophobic character which is attributed to its relatively low hydrophilic-lipophilic balance. The APG₁₄ which is having longer hydrophobic chain length was not soluble at 25°C whereas APG₁₂ can.

3.3.2 CRITICAL MICELLE CONCENTRATION

The CMC is the aqueous concentration of the surfactant at which the surfactant solution attain the smallest surface tension due to the micelle formation. Above the CMC, additional surfactants forms the aggregates in the bulk, whereas the concentration of the unassociated monomers remains constant. CMC values were determined from the break point between concentration and

Table 2 surface active properties of APG₁₂&APG₁₄.

Comp ound	CMC (mmol dm ⁻³)	γ_{CMC} (mNm ⁻¹)	Γ_{CMC} ($\times 10^{-6}$ molm ⁻²)	ΔG_{CMC} (kJmol ⁻¹)	A_{CMC} (nm ² mole ⁻¹)
APG ₁₂	0.29	32	3.9	31.27	0.44
APG ₁₄	0.07	30	3.7	31.26	0.49

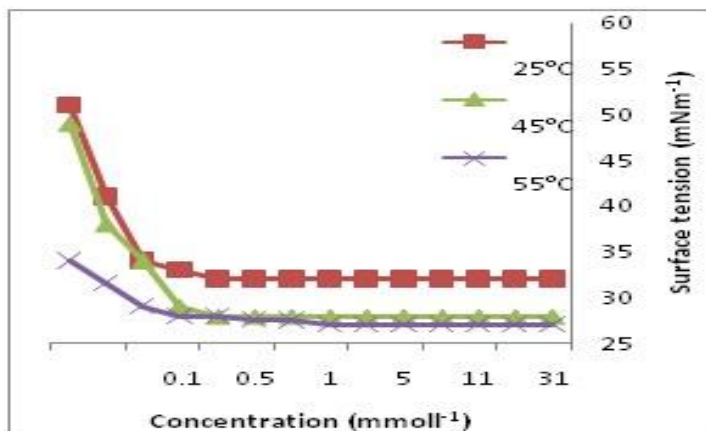


Fig - 2 Surface tension of APG₁₄ at different temperatures.

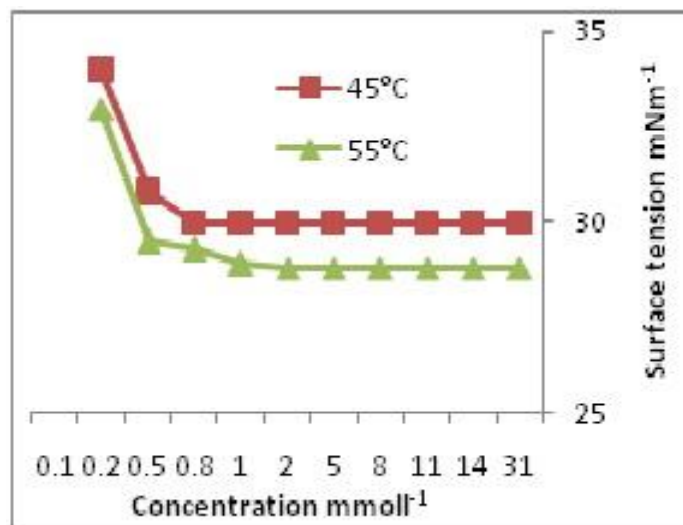


Fig - 1 Surface tension of APG₁₄ at different temperatures.

surface tension values. The hydrophobic moiety had a strong influence on CMC values. As seen in table 2 the CMC value decrease distinctly with increasing alkyl chain length. As a general approximation, the CMC value is lowered by a factor of 10 when the chain length is increased by two.

3.3.3 SURFACE EXCESS CONCENTRATION AND OCCUPIED AREA

The Gibbs equations have been used to calculate the area demand per molecule at the interface (A) from surface tension measurements. To calculate Γ_{CMC} and A_{CMC} it is usual to fit a polynomial (quadratic) to the pre-CMC data and calculate the derivative $d\gamma/d\ln C$ at the CMC. As can be seen in table 2, the excess concentration of surfactant increases as the length of the alkyl chain increases. These results indicate that the

increasing of the length of the alkyl chain produces a higher surface activity through lower CMC. The surface area demand per molecule for the APGs gives some information on the packing degree of adsorbed molecules. In the present study, the A_{CMC} value decreases with increasing chain length. This may indicate that the tight packing in the thickened adsorption layer, showed strong adhesion interaction.

3.3.4 BIODEGRADABILITY

Biodegradability testing plays an important role in the assessment of the environmental behavior of surfactants. The UV- VIS spectroscopic determination of APGs based on their reaction with the Anthrone reagent was used to determine the primary aerobic biodegradability [11]. It was observed that in the beginning the rate of degradation of

APG₁₄ was higher than that of the APG₁₂, after 4day the initial degradation of both the APGs were more than 70% (73% for

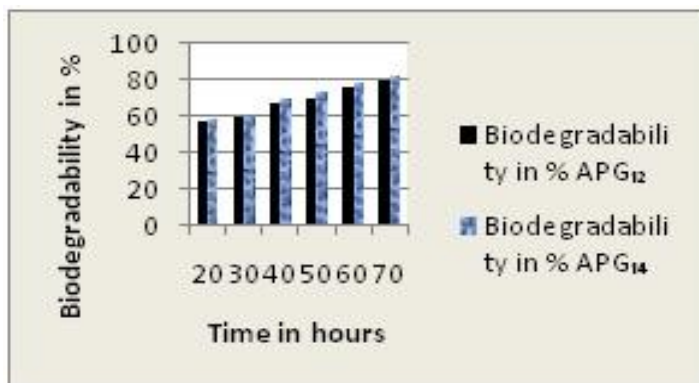


Fig - 3 Primary biodegradation of alkyl polyglucosides.

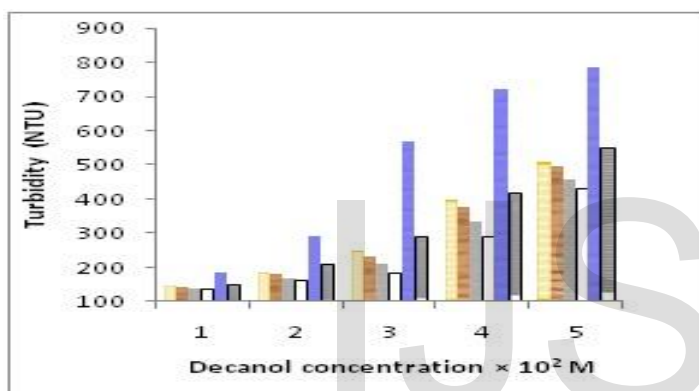


Fig - 4 Turbidity vs. concentration of decanol in SDS, APG₁₂ and mixture of the two (APG : SDS = 4:1, 3:2, 2:3 and 1:4) in different mole ratios.

APG₁₂ and 80% for APG₁₄). Current legislation requires a minimum level of biodegradation of over 80% for surfactants to be considered biodegradable, when the OECD test is

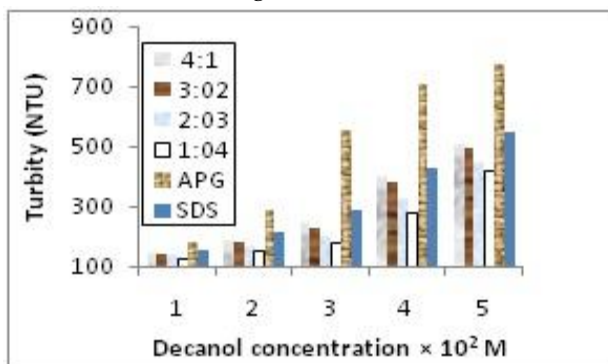


Fig - 5 Turbidity vs. concentration of decanol in SDS, APG₁₄ and mixture of the two (APG : SDS = 4:1, 3:2, 2:3 and 1:4) in different mole ratios.

applied. The synthesized APGs may therefore be considered as readily biodegradable under actual

environmental conditions. The rate of biodegradation of APG with sewage water under normal environmental condition is found similarity with the OECD result with slight changes. The trend of biodegradability for both APGs with time is given in Figure 2.

3.3.5 DISPERSING POWER OF APGs

The dispersing power has been analyzed in terms of turbidity. The turbidity shown in the figure 3, 4 have been calculated by measuring the turbidity of decanol with APG₁₂, decanol with APG₁₄ surfactant mixtures corrected by subtracting the background turbidity of the surfactant solution and the turbidity of decanol dispersion in water. The same method has been repeated for the decanol and SDS surfactant mixtures and decanol + APG₁₂ : SDS binary mixtures, decanol + APG₁₄ : SDS binary mixtures. The surfactant/decanol dispersion results show a general trend of increasing turbidity to a maximum value as decanol concentration increased. The turbidity get decreased with the change of molar ratio of the binary mixtures from 1:4 to 4:1 (SDS : APGs respectively). The observed increase of turbidity is due to the dispersion of decanol. Also, when the molar ratio has been changed from 1:4 to 4:1, the dispersed decanol get solubilized in turn it decrease the turbidity and prove the synergistic ability of APGs with SDS.

Table 3 Performance properties of APG₁₂ and APG₁₄.

Compound	Foam height			Emulsion stability (Sec)	Wetting time (Sec)
	Initial (ml)	Final (ml)	Foam stability (%)		
APG ₁₂	23.0	21.0	91	300	50
APG ₁₄	9.5	9.1	95	410	55

3.3.6 FOAMING, EMULSION STABILITY AND WETTING PROPERTIES

The foaming ability of the synthesized natural surfactants is given in Table 3. The foam height decreases as the alkyl chain length increases. The APG₁₂ surfactant showed better foam stability than the APG₁₄. The wetting time for APG₁₂ was 55 sec. It indicated that the APG₁₂ had better wetting ability than APG₁₄.

The data determined by standard methods [13] showed that the increase of hydrophilic chain length resulted in an increase in its emulsion stability. That may be due to the efficiency of adsorption from aqueous solution and an increase in its tendency to adsorb through its hydrophobic group.

4. CONCLUSION

The optimum molar ratio of the PTSA catalyst for the

synthesis of carbohydrate based APGs was concluded as 0.005 mole per mole of glucose. Further their surface active properties were determined by measuring equilibrium surface tension. The results showed that the synthesized APG surfactants provide an excellent surface activity such as lower CMC, lower surface tension and closer packing at the air/water interface than that of the other ionic surfactants. The synthesized surfactants showed a better biodegradability and the dispersion studies of APGs with SDS revealed very superior synergism in their performance.

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