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RESEARCH ARTICLE

Surfactant behaviour of five carbohydrate liquid crystals

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Abstract: The study of liquid crystalline behaviour of new amphiphilic carbohydrate derived liquid crystals has gained world-wide interest, since these glycolipids have technical and biological applications in a wide area such as thermotropic and lyotropic liquid crystals, surfactants, lubricants, solubilization and crystallization of membrane enzymes etc. Glycolipids are natural surfactants based on a hydrophilic sugar (carbohydrate) part and a hydrophobic hydrocarbon domain. In this paper, surfactant behaviour of five glycolipids is presented based on their critical micelle concentration (CMC). The nonionic surfactants treated with iodine, form donor–acceptor complexes in aqueous medium. Thus the CMC is determined by the spectral absorption and the shift in the absorbance maximum (λ_{max}) of I_2 upon complex formation with surfactants. For a better comparison of results, turbidity measurements were exploited to determine the CMC. In accordance with the results of both methods, the CMC of all the acetylated compounds lie within the typical range for nonionic surfactants; 10^{-5} – 10^{-4} mol dm^{-3}. Further, other fundamental parameters of surfactants, such as the HLB values and the cloud points of each compound were also studied.

Keywords: Cloud point, critical micelle concentration, glycolipids, hydrophilic lipophilic balance, surfactants.

INTRODUCTION

Since the discovery of liquid crystals over a century ago, the phenomena has been applied to many products in our society. Lyotropic mesophases differ highly from thermotropic mesophases, because the formation of these lyotropic phases, such as lamellar, hexagonal and cubic phases depends on the temperature, type of the solvent and the solute concentration (Smits *et al*., 1977). In carbohydrate derived liquid crystals, the carbohydrate part dissolves in water or in polar solvents while the hydrocarbon chain dissolves in non polar solvents forming supramolecular aggregates that collectively exhibit lyotropic mesophases. Most of the liquid crystals exhibiting these properties are nonionic surfactants (Jeffrey, 1986; Vill & Hashim, 2002). Carbohydrates linked with fatty acids, long chain alkanols and other hydrophobic moieties can be used as good alternatives to surfactants based on petrochemicals. Especially, alkylglycosides show widespread appli-cations both in research and industries based on cosmetics and hygienic products (Greffe *et al*., 2005).

Biosurfactants are biomolecules that can partition preferentially at interfaces with properties comparable to synthetic surfactants. Microorganisms are known to synthesize alkylglycosides (Holmberg, 2001), rhamnolipids, sophorolipids and lipopeptides having surfactant properties (Mulligan, 2005). At present, biosurfactants are predominantly used in remediation of pollutants. Emulsification, stabilization, antiadhesive and antimicrobial activities are properties of biosurfactants that come in useful in the food industry (Nitschke & Costa, 2007). Since biosurfactants are environmentally compatible, they have a greater commercial potential (Lin, 1996).

Amphiphilic compounds containing nonpolar tails and polar head groups within the same molecule possess surfactant properties. These are mainly organic substances, which are at least partially dissolved in water, thus lowering the surface tension significantly (Oremusová & Lengyel, 2007). Because of this nature, surfactants can be used in emulsification, surface wetting, frothing, solubilization and dispersion (Baker *et al*., 2001). Surfactants are also called surface active agents, because they form a thin monolayer mainly by the adsorption on to the surface of the solution.

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At low concentrations, surfactants are water soluble. However, at higher concentrations, surfactant molecules tend to self associate into thermodynamically stable molecular aggregates/complexes in aqueous solutions under specific environmental conditions. These molecular aggregates are known as micelles and the specific surfactant concentration at which the association of molecules begins is named as the critical micelle concentration (CMC) (Baker *et al*., 2001). The typical CMC for nonionic surfactants lies in between 10^{-5} –10^{-4} mol dm^{-3} (Hait & Moulik, 2001).

The determination of CMC by measuring micelle-influenced physical properties as a function of concentration has lead to more than 30 methods that are used in the recent past. Out of these methods, the most popular methods are tensiometry, conductometry, viscometry, fluorometry, calorimetry, spectrophotometry, nuclear magnetic resonance (NMR) spectroscopy and light scattering (Suzuki, 1970; Mysels & Mujerjee, 1979; Schramm & Marangoni, 2000; Hait & Moulik, 2001; Ghosh *et al*., 2003; Mihali *et al*., 2008). In this study, the UV absorption spectrum method and the turbidity measurement were used and results from each were compared.

Generally, in a surfactant molecule, there is a balance between the polar and the non polar part of the molecule. This balance depends on the molecular structure and the type of the molecule. In an amphiphilic molecule this relative ratio is called the hydrophilic- lipophilic balance or the HLB value, which is an arbitrary parameter used to categorize surfactants as detergents, emulsifiers, solubilizers, wetting agents, etc. The generally used method to compute the HLB value is using the chemical formulae of surfactants created by Griffin (Hait & Moulik, 2001; Haw, 2004). According to that, HLB value is taken as the molecular weight percent of the hydrophilic or water loving part of the nonionic surfactant divided by five (equation 1).

$$\text{HLB} = (\text{Percent relative molecular mass of hydrophilic group}) / 5 \quad ...(01)$$

The working scale used for the surfactants is from 0.5 to 19.5 or 20.0 (Hait & Moulik, 2001; Haw, 2004).

The definition of cloud point (T_c) varies depending on the type of the surfactant. For anionic surfactants, T_c is the temperature at which the surfactant solution becomes turbid when it is cooled under specific conditions, whereas for nonionic surfactants, T_c is the temperature at which the solution becomes turbid when heated. The cloud point can be measured by observing the turbidity of a 1 % (by mass) surfactant solution, as a function of temperature (Schramm & Marangoni, 2000).

Strategies for development of carbohydrate linked lipids for use as surfactants is an area for future consideration. The linkage of various lipids to carbohydrates has given a series of compounds, some of which, we have previously studied for their liquid crystalline behaviour (Abeyrathne *et al*., 2012). The present study, reports the surfactant behaviour of five liquid crystalline acetylated glycosides. The surfactant property of the compounds has been determined by the measurement of the CMC value using spectral absorption and the shift in the absorbance maximum (λ_{max}) of I_2 upon complex formation with surfactant. These CMC values were compared with the CMC values obtained from the turbidity measurements. Further, other fundamental parameters of surfactants, such as the HLB values and the cloud points of each compound were also studied.

METHODS AND MATERIALS

Instrumentation

The chemical structures of five glycolipids used in the present study are shown in Figure 1. The synthesis and characterization of compounds A, B and C have been reported previously (Abeyrathne *et al*., 2012). The synthesis and characterization of compounds D and E are given below. All the reagents and solvents were purchased and some were purified before use. The chemical structures of glycolipids D and E were confirmed by spectroscopic techniques; NMR spectroscopy (300 MHz Varian VTR-300 spectrometer); chemical shifts are relative to $CDCl_3$, infrared spectra were recorded on a FTIR spectrometer (IR Prestige- 21, SHIMADZU) and mass spectra were obtained using GC-MS spectrometer (Varian 2000, SATURN GC/ MS/ MS).

Synthesis of glucosides

Synthesis of 3-epiandrosteryl-2, 3, 4, 6-tetra-O-acetyl-β-D-glucopyranoside (D)

3-β-epiandrosterone (1.09 g), tetra-O-acetyl-β-D-glucopy-ranosyl chloride (0.55 g), powdered anhydrous calcium sulphate (0.62 g) and dried, finely powdered silver oxide (0.38 g) were added into ether (5 mL) and stirred for 24 h at room temperature in a dark place. The solids were removed by filtration and ether was evaporated. The remaining residue was dissolved in a small amount of dichloromethane and stirred overnight in methanol. Finally, the product was collected by filtration and washed with cold methanol.

Yield; 0.15 g (65 %), Mass; *m/z* { M^+ (cal = 620), 590, 506, 504, 429, 331, 272}, FTIR; ν_{max}/ cm^{-1} = 1730.15 (C=O), 2929 (CH), 1516 (CH_3), 1000-1300 (C-O), 600- 1500 (sugar part). ^{1}H-NMR (300 MHz, $CDCl_3$); δ = 2.02- 2.06 (4 s, 12 H, 4 × acetyl), 5.70 (m, 1 H, H-5), 4.09, 4.29 (d, 1 H, H-6), 6.32 (d, 1-H, H-1), 5.11, 5.19, 5.41 (3 dd, 3 H, H-2, 4, 3), 0.82- 0.84 (2 s, 6H, 2× CH_3), 1.0- 2.0 (2 m, C-H). ^{13}C-NMR ($CDCl_3$); δ = 20.62 (q, 5 × CH_3), 169.16, 169.81, 170.07, 170.64 (4 s, CO acetyl), 89.29 (d, C-1), 70.06 (d, C-2), 70.04 (d, C-4), 69.43 (d, C-3), 68.15 (d, C-5), 221.46 (s, C=O), 12.51 (q, 1 × CH_3), signals in the range δ = 20 − 60 are due to the ring carbon atoms of epiandrosteryl skeleton. Mp; 80 − 110 ˚C.

Synthesis of penta cinnamyl-α-D-glucopyranoside (E)

D-glucose (1.0 mmol, 0.18 g) was reacted with cinnamyl alcohol (9.7 mmol, 1.3 g) by stirring for 24 h in dioxane (3.6 mL) and p-toluene sulfonic acid monohydrate (0.17 mmol, 0.032 g), followed by neutralization with ammonia solution and evaporation of volatile compounds. The residue was filtered through silica gel (9:1 ethylacetate : ethanol) and 0.48 g of hydrated penta-cinnamyl-α-D-glucopyranoside was obtained as white needles.

Mass; *m/z* {M^+ (cal = 662.8), 613.9, 568.0, 541.0, 527.2, 411.1, 396.1,306.2}, FTIR; ν_{max}/ cm^{-1} = 3104.88 (C-OH), 1625 (C=C), 1402.02 (arom H), 1172.53 (C-O-R), 600-1500 (sugar part). ^{1}H; δ = 2.22 (s, 1 H, OH), 4.54 (m, 1 H, H-5), 4.44 (d, 1 H, H-6), 4.61 (d, 1-H, H-1), 4.47-5.01 (3 dd, 3 H, H-2, 3, 4), 7.18 - 7.53 (m, 20H). ^{13}C; δ 100.99 (d, C-1), 82.13 (d, C-2), 81.01 (d, C-4), 78.55 (d, C-3), 64.77 (d, C-5), 55.62 (d, C-1′), 129.27 (d, C-2´), 139.77 (d, C-3´), 141.43 (s, arom C), 128.65-125.12 (m, arom CH). Mp; 318.6 ˚C.

Measurement of CMC

The general procedures used for the determination of critical micelle concentration (CMC) of glycolipids are described below.

Method 1: UV- absorption spectroscopy

The spectral measurements were carried out with an ultraviolet (UV) - visible spectrophotometer (UV – 1601; SHIMADZU), using a pair of quartz cells having a path length of 1 cm. All the measurements were taken at room temperature (298 K).

Note: Multiple testing of surfactant solutions was performed to maintain consistency in readings.

A stock solution (0.025 mol dm^{-3}) of each acetylated compound (A – D in ethanol and E in methanol) was prepared and diluted for measurements to a concentration range between 0.25 – 5.0 x10^{-4} mol dm^{-3}. A saturated aqueous solution of iodine at 25 ˚C (2.5 cm^3) was poured into each of the marked and stoppered test tubes (10 cm^3), and varying amounts of the stock solution were added and made up to a volume of 10.0 cm^3 with distilled water (Hait & Moulik, 2001). UV spectra of all the solutions were obtained from 250 – 500 nm at room temperature. The maximum absorbance value at λ_{max} of I_2 in each solution was measured to study the blue shift with increasing concentration. The absorbance value at 286, 346 and 460 nm wavelengths of each solution was also measured.

Method 2: Turbidity measurements

The turbidity of each solution was measured using a digital nephlo-turbidity meter (2100 P/ HACH) in nephelometric turbidity units (NTU). The instrument was calibrated using standard solutions supplied with the instrument before taking the measurements. Here also multiple testing of surfactant solutions was performed to maintain the consistency in readings.

A series of concentrations of all acetylated solutions were prepared by the dilution of each stock solution (2.0 mmol dm^{-3}) with distilled water. The stocks were constituted in acetonitrile (A and C), ethanol (B and D) or acetone (E). The concentrations of the diluted stocks ranged from 0.25 x 10^{-4} mol dm^{-3} to 1 x 10^{-3} mol dm^{-3}. The turbidity of each solution was measured at room temperature in triplicate at 30 s intervals.

Determination of cloud point

A 1 % aqueous solution of each acetylated compound was heated on a hot plate and monitored for haziness or cloudiness. The temperature at which the first haze was observed was taken as the cloud point of that compound.

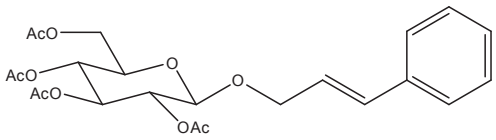
RESULTS AND DISCUSSION

In carbohydrate derived liquid crystals, the carbohydrate part dissolves in water or in polar solvents while the hydrocarbon chain dissolves in non polar solvents forming supramolecular aggregates that collectively exhibit lyotropic mesophases and most of these liquid crystals are nonionic surfactants (Baker *et al.*, 2001). This is mainly due to the amphiphilic nature of the molecule. The synthesized glycosides clearly show amphiphilic

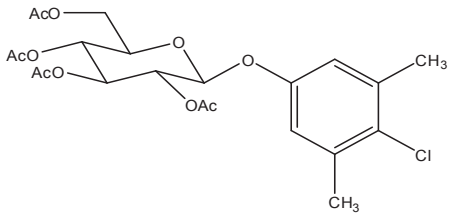
properties and may self associate into micelles at specific environmental conditions functioning as nonionic surfactants.

The CMC is one of the fundamental properties of surfactants at which the surfactants show a distinct change in their physical properties. At a specific, narrow concentration range known as the critical micelle concentration (CMC), surfactant molecules tend to self associate into thermodynamically stable molecular aggregates/ complexes (micelles) in aqueous solutions. Physical properties such as surface tension, absorbance and turbidity show drastic changes at this point. In accordance with that, the determination of CMC by UV –visible spectrophotometry and the turbidity method have been used in the estimation of surfactant property of these novel compounds.

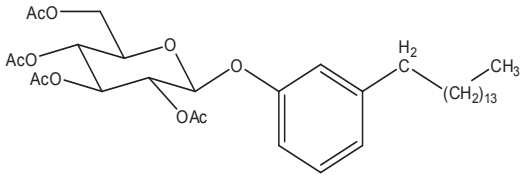
(A) cinnamyl 2, 3, 4, 6-tetra-O-acetyl-β-D-glucopyranoside



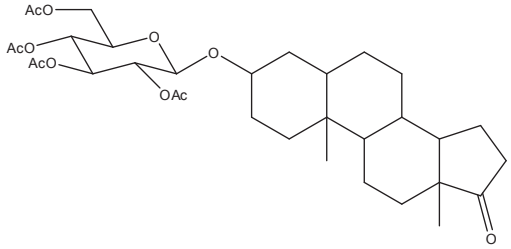
(B) 4-chloro-3, 5-dimethylphenyl 2, 3, 4, 6-tetra-O-acetyl-β-D-glucopyranoside



(C) 3-pentadecylphenyl-2, 3, 4, 6-tetra-O-acetyl- β -D-glucopyranoside



(D) 3-epiandrosteryl -2, 3, 4, 6-tetra-O-acetyl- β -D-glucopyranoside



(E) pentacinnamyl-β-D-glucopyranoside

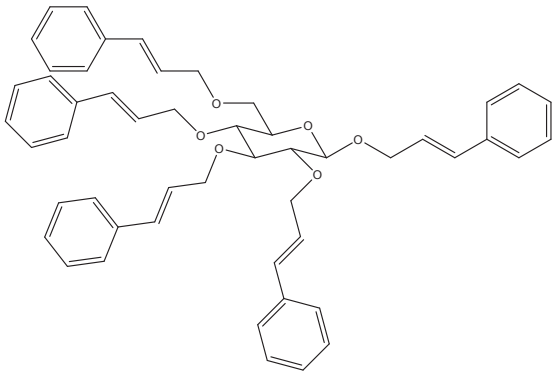


Figure 1: Chemical structures of glycolipids synthesized

Method 1: UV absorption spectroscopy

The UV-visible spectrophotometric studies were conducted to determine the CMC of the acetylated glucosides. The nonionic surfactants form donor-acceptor complexes with iodine in aqueous solutions leading to shifts in the absorbance maximum (λ_{max}) and changes in spectral absorption, which are used here to determine the CMC point. The formation of the donor-acceptor complex is mainly due to the fact that nonionic surfactants have the ability to serve as iodophores or I_2 carriers without loosing their surfactant properties (Hait & Moulik, 2001). Iodine shows three absorbance maxima at 286, 346 and 460 nm in the absorbance spectrum (Figure 2 curve 1). When I_2 is complexed with a non-ionic surfactant, shifts in these absorbance maxima can be observed at different surfactant concentrations (Figure 2 curves 2-6). This complexation results in a blue shift of the absorption maxima. Hence, absorbance of the synthesized acetylated compounds was obtained at these three absorbance maxima (Figure 2). Although the bond between I_2 and nonionic surfactant is not well explained in literature yet, the blue shift of the λ_{max} may be due to the ability of the ether oxygen, linking the anomeric carbon to the aglycone part in the glycoside to donate electrons to the vacant σ* orbital of iodine resulting in the complex. The extent of the shift depends on the molecule itself (Suzuki, 1970; Patist *et al*., 2000; Hait & Moulik, 2001).

For the compound A, the plot of absorbance at three wavelengths 286, 346 and 460 nm *vs* the concentration of the compound (Figure 3a) showed distinct break points at 0.195 mmol dm^{-3}, 0.214 mmol dm^{-3} and 0.216 mmol dm^{-3}, respectively, which is considered as the corresponding CMC values of that compound. The absorbance *vs* concentration plots for compounds B, D and E show similar break points whereas, for compound C, CMC is considered as the point where the curves show a sudden drop of absorbance.

According to the spectra of I_2 from 250 nm to 500 nm in the absence and presence of compound A (Figure 2), shifts in the λ_{max} of iodine at 460 nm to lower wave lengths and an increase in the absorbance were observed with increasing concentration of the compounds, resulting in a blue shift. This type of blue shift is observed at 286 nm and 346 nm wavelengths too, but the extent of the shift is different at these three different wavelengths. In Figure 2, the concentrations plotted are above the CMC point of the compound A. The other compounds B – E also show similar blue shifts in λ_{max} with increasing concentrations.

Method 2: Turbidity measurements

The turbidity method is used for comparison of the CMC values obtained from the UV-absorption spectra method. Turbidity is the measurement of the degree of opacity in a suspension and it is measured using a digital nephlo-turbidity meter (Sandhu & Robbins, 1993; Homendra & Devi, 2004). The measurement is based on the amount of scattered light in the solution, which is called the Tyndall effect (Bakshi & Sood, 2004; Homendra & Devi, 2004). Here, the intensity of a transmitted and diffused monochromatic light at 90° by the solution is measured and its ratio in Nephlo turbidity units (NTU) is taken as the turbidity (Ciaccheri & Mignani, 2008).

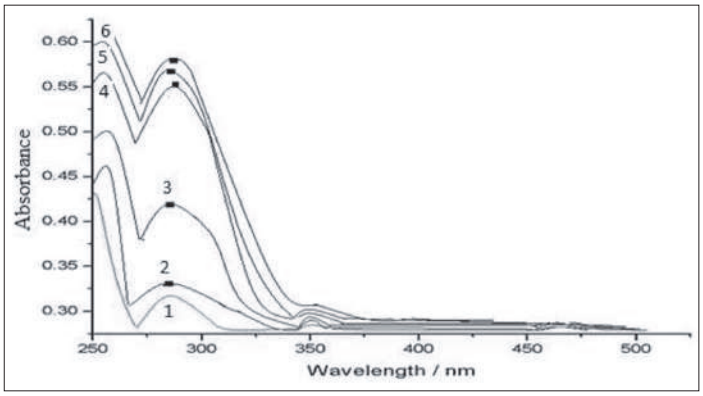


Figure 2: Absorbance spectra of compound A and I_2 at room temperature. Curve (1) I_2 only and curves (2) – (6), I_2 and [A] = 0.25×10^{-4}, 0.5×10^{-4}, 0.75×10^{-4}, 1.50×10^{-4}, 2.00×10^{-4} mol dm^{-3}, respectively.

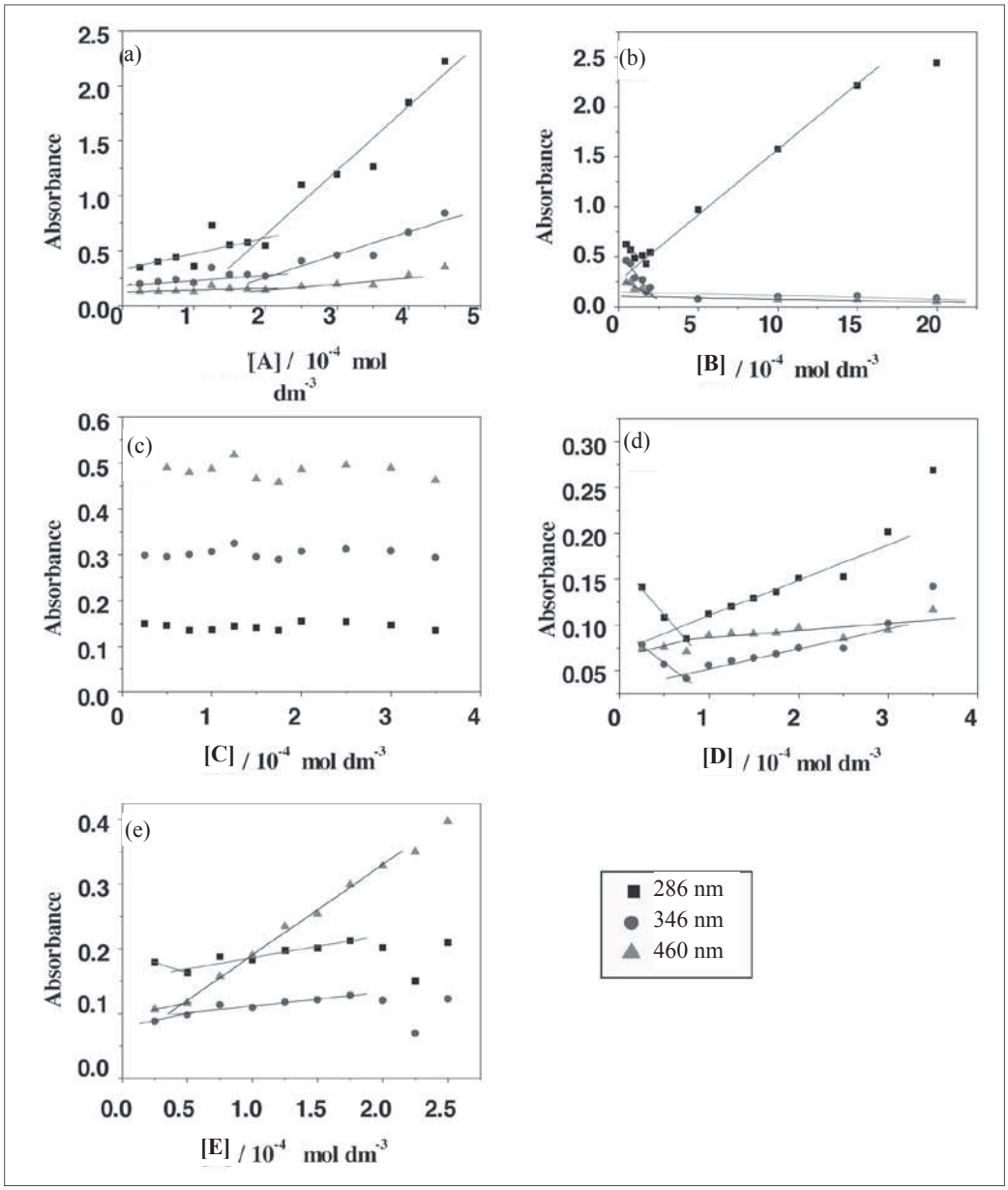


Figure 3: The plot of absorbance *vs* concentration of I_2 and (a) A; (b) B; (c) C; (d) D and (e) E at wavelengths of 286, 346 and 460 nm at room temperature. The intersection point in each plot is the CMC point

A series of concentrations of surfactant solutions of acetylated glucosides were made with the stock solution of the respective glucoside and distilled water. The compounds A and C in solutions gave a turbid appearance with increasing concentration (Figures 4a and 4b) whereas for compounds B, D and E, a turbid appearance was not visually observed as shown in Figure 4c, although they gave significant turbidity measurements.

The plot of turbidity *vs* surfactant concentration of each compound is given in Figure 5. The CMC value is taken at the first point of inflexion. All the compounds except for compound C showed two breaking points. Most surfactants are reported to show two points of inflexion (Oremusová & Greksakova, 2003) with Tween 20 having only one such point. The CMC values obtained from the breaking points of the UV-absorption plot and turbidity plot of each compound are compared in Table 1.

According to Table 1, the CMC values obtained by the characteristic plots of turbidity *vs* concentration (Figure 5) were slightly lower, but closely agreed with those obtained from the UV absorption method. Turbidity is a function of particle size, which varies from sample to sample, because it depends on the solvent medium and the severity of damage. Thereby, it should be noted that the CMC of a surfactant varies to some extent with the solution properties that are measured and the evaluation method used (Doong *et al*., 1996; Patist *et al*., 2000). All these CMC values lie in the typical CMC value range of nonionic surfactants.

HLB value is one of the fundamental properties of a surfactant by which its applicability can be determined. The HLB value gives an indication about the solubility of the surfactant and according to that value, the application of a certain surfactant can be decided easily (Haw, 2004). In general, low HLB values indicate that the surfactant is

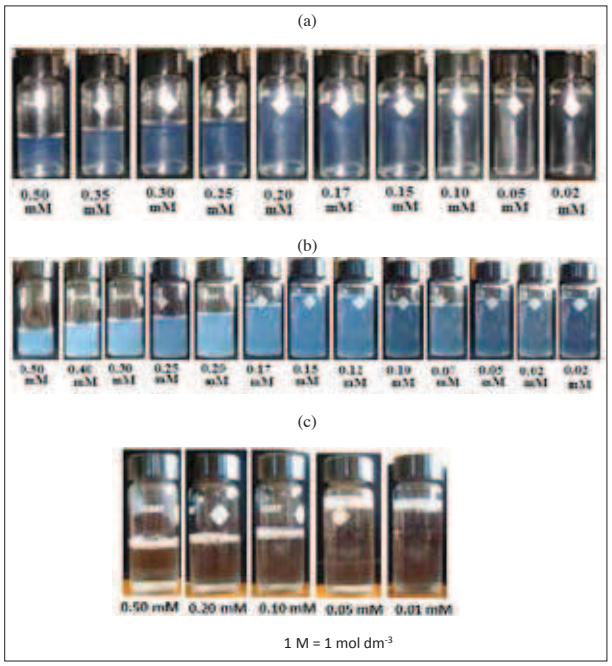


Figure 4: The variation of turbidity in a series of concentrations of compound (a) A; (b) C; (c) D at room temperature

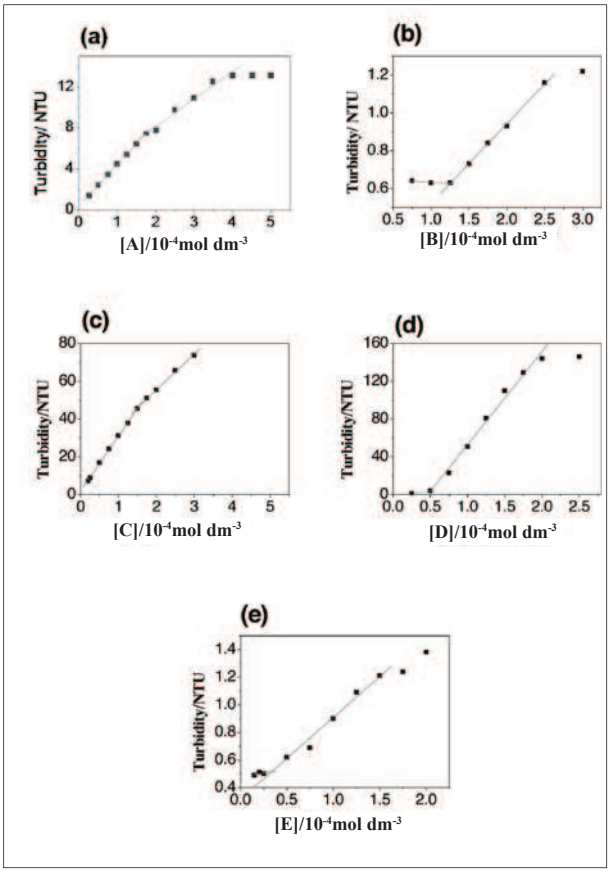


Figure 5: The plot of turbidity *vs* glucoside concentration (a) A; (b) B; (c) C; (d) D and (e) E

Table 1: CMC values obtained for compounds A – E

Compound	CMC by UV absorption measurement / mmol dm^{-3} Wavelength/ nm			CMC by turbidity measurement / mmol dm^{-3}
	286	346	460	
A	0.195	0.214	0.216	0.176
B	0.167	0.173	0.179	0.125
C	0.161	0.161	0.161	0.151
D	0.063	0.064	0.068	0.050
E	0.044	0.045	0.049	0.034

more lipophilic and can stabilize water-in-oil emulsions. Larger HLB values are indicative of greater hydrophilicity of the surfactant and their preference for stabilizing oil-in-water emulsions. The HLB values calculated for the acetylated glucosides are given in Table 2. The surfactant is more water soluble if the HLB value is higher and it is more oil soluble if the HLB value is lower. The HLB values of compounds A, B, C and D lies within the range of 8 to 15 and hence they can be used as good stabilizers for oil-in-water emulsions, whereas that of the compound E lies within the range of 3 to 6 and hence it can be applied to stabilize water-in-oil emulsions. Also the HLB values of compounds A and B lies within the HLB range of 13 to 15 and can be used to make detergent solutions.

Upon heating an aqueous solution (1 % by mass) of a nonionic surfactant, the colour of the solution goes from clear to white or turbid and this is reversible upon cooling. The temperature at which the first haze is observed is considered as the cloud point. The turbidity observed in the solution is mainly due to the growth of micelles, which are large enough to scatter light and it is important to determine the cloud point in order to get an idea on the phase separation for most applications. Cloud points observed for each of the compounds A, B, C and D are given in Table 2.

For the compound E, haziness upon heating was not observed, which may be attributed to the much higher melting point of that compound, 318.6 ˚C. Since the compound is heated in water, the temperature cannot exceed 100 ˚C due to the evaporation of the solvent.

The observed cloud points lie within a narrow temperature range.

Table 2: Calculated HLB values, observed melting points and cloud points and the corresponding molecular weights of acetylated glucosides

Compound	Molar mass/ g mol $^{-1}$	Melting point/ ^{o}C	Cloud point/ ^{o}C	HLB
A	464.0	83.0	45 − 50	14.96
B	486.6	98.0	48 − 55	14.26
C	634.0	64.0	53 − 55	10.95
D	620.0	110.0	65 − 70	11.19
E	778.0	318.6	Not determined	4.49

CONCLUSION

The synthesised glycosides show amphiphilic properties with the ability to self associate into micelles and demonstrate properties of nonionic surfactants. The characteristic plots of absorbance at three different wavelengths *vs* concentration of the acetylated compounds showed a distinct intersection point corresponding to the CMC value of each surfactant. These values lie in-between the typical CMC for nonionic surfactants; $10^{-5} – 10^{-4}$ mol dm^{-3} (Schramm & Marangoni, 2000). Blue shifts in the absorbance maxima of the iodine complexes with varying surfactant concentration was observed at different wave lengths. According to the results, the CMC values obtained from the plots of turbidity *vs* concentration were slightly different but were in close agreement with those obtained from the UV absorption method. This variation caused in the CMC of a surfactant is attributed to the measured solution property and method of evaluation used. Theoretically, for a fixed polar moiety of a nonionic surfactant, an increase in the length of the nonpolar part results in a decrease in the CMC of the compound. Thus compound C with its long hydrocarbon tail, has a CMC of 0.16 mmol dm^{-3}, whereas compound A, with a much shorter hydrophobic part has a CMC of 0.20 mmol dm^{-3} by UV absorption measurement. A similar observation is seen with compounds C (0.16 mmol dm^{-3}) and D (0.17 mmol dm^{-3}).

The HLB values of compounds A, B, C and D indicate that they can be used as good stabilizers for oil-in-water emulsions whereas that of the compound E is typical of emulsifiers stabilizing water-in-oil emulsions. Also the HLB values of compounds A and B lie within the HLB range of 13 to 15 and can be used to make detergent solutions.

Although the surfactant behaviour of deacetylated compounds were not studied, from their molecular structure and the results obtained for the acetylated compounds, it is possible that they also possess properties of nonionic surfactants.

Acknowledgement

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REFERENCES

1. Abeyrathne A.R.N.M., Perera A.D.L.C & Karunaratne D.N. (2012). Liquid crystal behaviour of three novel glycosides. *Journal of the National Science Foundation of Sri Lanka* **40** (2): 115 − 121. DOI: *http://dx.doi.org/10.4038/jnsfsr.v40i2.4439*
2. Baker G.A., Bright F.V. & Pandey S. (2001). Quantifying critical micelle concentration and non-idealities within binary mixed micellar systems: an upper level undergraduate laboratory. *Chemical Educator* **6** (4): 223 − 226. DOI: *http://dx.doi.org/10.1007/s00897010487a*
3. Bakshi M.S. & Sood R. (2004). Head group controlled specific interactions of aliphatic- and aromatic-polyester dendrimers with cationic surfactants of identical hydrophobic tails. *Colloids and Surfaces A: Physicochemical Engineering Aspects* **244**: 159 − 168. DOI: *http://dx.doi.org/10.1016/j.colsurfa.2004.06.021*
4. Ciaccheri L. & Mignani A.G. (2008). Scattered colorimetry and multivariate data processing as an objective tool for liquid classification and mapping. *Current Analytical Chemistry* **4**: 371. DOI: *http://dx.doi.org/10.2174/157341108785914899*
5. Doong R., Lei W., Chen T., Lee C., Chen J. & Chang W. (1996). Effect of anionic and nonionic surfactants on sorption and micellar solubilization of monocyclic aromatic compounds. *Water Science Technology* **34** (7-8): 327 − 334. DOI: *http://dx.doi.org/10.1016/S0273-1223(96)00761-5*
6. Ghosh S.K., Khatua P.K. & Bhattacharya S.Ch. (2003). Aggregation of non ionic surfactant igepal in aqueous solution: fluorescence and light scattering studies. *International Journal of Molecular Sciences* **4***:* 562 − 571. DOI: *http://dx.doi.org/10.3390/i4110562*
7. Greffe L., Bessueille L., Bulone V. & Brumer H. (2005). Synthesis, preliminary characterization and application of novel surfactants from highly branched xyloglucan oligosaccharides. *Glycobiology* **15** (4): 437 − 445. DOI: *http://dx.doi.org/10.1093/glycob/cwi013*
8. Hait S.K. & Moulik S.P. (2001). 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. *Journal of Surfactants and Detergents* **4**(3): 303 − 309. DOI: *http://dx.doi.org/10.1007/s11743-001-0184-2*
9. Haw P. (2004). The HLB system; a time saving guide to surfactant selection. Presentation to the Midwest chapter of the society of cosmetic chemists. Available at *http://www.lotioncrafter.cpm/pdf/The_HLBsystem.pdf*, Accessed 20 September 2011.
10. Holmberg K. (2001). Natural surfactants. *Current Opinion in Colloid & Interface Science* **6** (2): 148 − 159. DOI: *http://dx.doi.org/10.1016/S1359-0294(01)00074-7*
11. Homendra N. & Devi I.C. (2004). Turbidity studies on mixed surfactant systems in hard water: a new method for estimation of water hardness. *Indian Journal of Chemical Technology* **11**: 783 − 786.
12. Jeffrey G.A. (1986). Carbohydrate liquid crystals. *Accounts of Chemical Research* **19**: 168. DOI: *http://dx.doi.org/10.1021/ar00126a002*
13. Lin S.C. (1996). Biosurfactants: recent advances. *Journal of Chemical Technology and Biotechnology* **66** (2): 109 − 120. DOI: *http://dx.doi.org/10.1002/(SICI)1097-4660(199606)66:2<109::AID-JCTB477>3.0.CO;2-2*
14. Mihali C., Oprea G. & Cical E. (2008). Determination of critical micellar concentration of anionic surfactants using surfactants –sensible electrodes. *Chemistry Bulletin Politechnica* **53** (67): 1 − 2, 159 − 162.
15. Mulligan C.N. (2005). Environmental applications for biosurfactants. *Environmental Pollution* **133** (2): 183 − 198. DOI: *http://dx.doi.org/10.1016/j.envpol.2004.06.009*
16. Mysels K.J. & Mujerjee P. (1979). Reporting experimental data dealing with critical micellization concentrations (c.m.c's) of aqueous surfactant systems. *Pure and Applied Chemistry* **51**:1083 − 1089. DOI: *http://dx.doi.org/10.1351/pac197951051083*
17. Nitschke M. & Costa S.G.V.A.O. (2007). Biosurfactants in food industry. *Trends in Food Science & Technology* **18** (5): 252 − 259. DOI: *http://dx.doi.org/10.1016/j.tifs.2007.01.002*
18. Oremusová J. & Greksakova O. (2003). Methods for surfactant critical micelle/micellar concentration (CMC) determination. *Chemical Communications* **40**: 90 − 95.
19. Oremusová J. & Lengyel A. (2007). *Critical Micelle Concentration of Ionic Surfactants*. Available at *http://www.fpharm.uniba.sk*, Accessed 10 January 2012.
20. Patist A., Bhagwat S.S., Penfield K.W. & Shah D.O. (2000). On the measurement of critical micelle concentrations of pure and technical-grade nonionic surfactants. *Journal of Surfactants and Detergents* **3** (1): 53 − 57. DOI: *http://dx.doi.org/10.1007/s11743-000-0113-4*
21. Sandhu S.S. & Robbins C.R. (1993). A simple and sensitive technique based on protein loss measurements, to assess surface damage to human hair. *Journal of the Society of Cosmetic Chemists* **44**: 173.
22. Schramm L.L. & Marangoni D.G. (2000). Surfactants and their solutions: basic principles. *Surfactants: Fundamentals and Applications in the Petroleum Industry* (ed. L.L. Schramm), chapter 1, pp. 3 − 51. Cambridge University Press, UK.

23. Smits E., Engberts J.B.F.N., Kellogg R.M. & van Doren H.A. (1997). Thermotropic and lyotropic liquid crystalline behaviour of 4-alkoxyphenyl β-D-glucopyranosides. *Liquid crystals* **23** (4): 481 − 488.
DOI: *http://dx.doi.org/10.1080/026782997208064*
24. Suzuki H. (1970). Determination of critical micelle concentration of surfactant by ultraviolet absorption spectra. *Journal of the American Oil Chemists' Society* **47**: 273 − 277.
25. Vill V. & Hashim R. (2002). Carbohydrate liquid crystals: structure-property relationship of thermotropic and lyotropic glycolipids. *Current Opinion in Colloid and Interface Science* **7**: 395 − 409.
DOI: *http://dx.doi.org/10.1016/S1359-0294(02)00091-2*