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Hexadecyl-β-D-Glucopyranoside: A Liquid Crystal with Surfactant Properties for Stabilization of Microemulsions

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Lyotropic liquid crystals (LLC) having amphiphilic properties are promising materials as co-surfactants in emulsion formulations. A carbohydrate lyotropic liquid crystal, hexadecyl-β-D-glucopyranoside, was synthesized by linking D-glucose to cetyl alcohol via acetylated glucoside and its ability to stabilize microemulsions was investigated. The synthesized compound was characterized by using Nuclear Magnetic Resonance Spectroscopy (NMR) and Fourier Transform Infrared Spectroscopy (FTIR). Both acetylated and deacetylated compounds were found to exhibit thermotropic and lyotropic liquid crystal behavior. The critical micelle concentration (CMC) value of 1.53 × 10^{-5}mol dm^{-3} obtained for hexadecyl-β-D-glucopyranoside from both UV-visible spectroscopic and turbidity methods suggests its non-ionic surfactant properties. Calculated HLB value of 8.86 indicates that it is suitable for making self-emulsifying oils and water in oil (W/O) emulsions. By introducing optimum amount of 0.05 wt% of newly synthesized hexadecyl-β-D-glucopyranoside as a co-surfactant, macro emulsions formulated with olive oil, water and non-ionic lipophilic surfactant sorbitan monostearate (Span 80) was successfully converted into microemulsions.

Introduction

Currently, "sugar-based surfactants" such as alkyl (poly) glycosides and sucrose fatty acid esters are being manufactured, [1] and play important roles in the surfactant & detergent industry. The industrial interest of these surfactants lie in the fact that they can be synthesized from renewable resources, for example glucose from starch and fatty alcohol from vegetable oils. In addition to the functionality and environmental compatibility, glycolipid bio-surfactants are directly produced by microbial processes from renewable resources. Thus, they have a great potential as "environmentally advanced surfactants" as well as sugar-based surfactants [2]. The selection of a surfactant should be based on its application because the solubility of the surfactant within the system affects its performance. The HLB (Hydrophilic Lipophilic Balance) value, the relationship between the hydrophilic portion

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and the lipophilic portion of the surfactant is an indicator for the prediction of solubility of non-ionic surfactants. Thus, the behavior of the surfactant can be expressed by the HLB value. Surfactants with higher HLB values form oil in water emulsions (O/W) because they are more likely to dissolve in water. Emulsifying agents with lower HLB values are suitable for water in oil emulsions (W/O) [3–6]. The HLB value for non-ionic surfactant can be calculated as follows.

$$\text{HLB value} = \frac{\left(\frac{\text{Molecular weight of water loving portion}}{\text{Total molecular weight of the surfactant}}\right)}{5} \quad (1)$$

Most surfactant materials show liquid crystalline properties.

Microemulsion systems are defined as thermodynamically stable systems which contain water and oil microstructures due to existence of surfactant film at the oil water interface [7]. Depending on the dispersed phase, microemulsions can be categorized as W/O (Water in oil) and O/W (Oil in water) emulsions. Basic components in a microemulsion system are oil, water, emulsifying agent (surfactant) and more frequently co-surfactant which can be a long chain alcohol, fatty acid, glycolipids etc. [6].

Micellar solution is the simplest form of self-assembled system. It is a single phase, homogeneous and amphiphilic system. Spontaneous organization of amphiphiles is quite interesting because they inherently consist of both polar and nonpolar characteristics. Continuous addition of amphiphiles into the aqueous solution leads to formation of micelles at a specific concentration in the system. This specific concentration is called "Critical Micelle Concentration" (CMC) [4]. According to Gibbs adsorption isotherms when the concentration of the amphiphiles is increased in the region before the CMC point, the surface tension of the solution is decreased. Even if the concentration of the amphiphiles is increased the surface tension of the solution remained constant in the region after the CMC point [5]. Iodine complex based method and turbidity method were carried out to observe the CMC value of synthesized glycolipid [3].

The aim of this research is to investigate a carbohydrate lyotropic liquid crystal having surfactant properties and stabilize its ability to form microemulsions and stabilize unstable macro emulsions. The influence of different polar and non-polar solvent systems on the self-assembly of *hexadecyl-β-D-glucopyranoside* was extensively studied by observing liquid crystalline textures. Thermotropic behavior of the synthesized compound was also studied. Ternary phase diagrams were constructed for olive oil/water/Span 80 systems at 70°C and room temperature by observing the morphology. In the study, some compositions of macroemulsions and unstable emulsions with phase separation were selected from the constructed ternary phase diagrams. Span 80 (nonionic surfactant) was used for the study and the amount of the surfactant was maintained below 10% in the formulations to avoid skin irritation [7,8]. Newly synthesized *hexadecyl-β-D-glucopyranoside* was introduced as a co-surfactant. Macro emulsions and unstable emulsions could be successfully converted into microemulsions by introducing 0.05 wt% of the compound.

Materials and Methods

Materials

All chemicals used were purchased from BDH Chemicals Ltd. All solvents were distilled prior to use.

Instrumentation

FTIR spectroscopic analysis was done at 25°C using infrared spectrophotometer (IR-PRESTISE -21,SHIMADZU) with pure KBr as the blank. Melting points of the synthesized products were measured using melting point apparatus (SMP1, Stuart Scientific, UK). Proton NMR spectroscopy was carried out using 300 MHz Varian VTR-300 spectrometer. Turbidity of solutions was measured using a digital nephlo-turbidity meter (2100 P/ HACH) in nephelometric turbidity units (NTU). The polarized light optical micrographs were taken with a polarized light microscope (Euromex, Holland) at room temperature. Silverson SL2 Laboratory Emulsifier was used for the formulation of emulsions. Centrifuge model (SIGMA -3 30 KS, Germany) was used for centrifuge purposes. Refractive indices were measured using a refractometer (HILGER WATTS, England).The conductivity measurements were performed with a conductivity meter (WPA CM 3J Linton, Cambridge) at 25°C. X-ray analysis was done using the X-ray diffractometer D-5000 (Siemens, Germany); 2θ range from 2.0° to 20.0° at 1.5406 A° wavelength with a scan rate of 0.0001°/ min and step size of 7 S.

Synthesis of Penta-O-Acetyl-β-D-Glucopyranoside

Anhydrous finely powdered sodium acetate (33.0 mmol) was added to acetic anhydride (27.7 mmol) contained in a 100 ml round bottom flask. The flask was fitted with a reflux water condenser and heated on a water bath at 90°C; which was the optimized temperature for the reaction. After sodium acetate was completely dissolved, finely powdered D-glucose (27.0 mmol) was added and heated for 3 hours. The mixture was poured into ice water with ice cubes, stirred vigorously and allowed to stand for 20 min at room temperature. The solid obtained was filtered and recrystallized from methylated spirit. The experimental yield was 47.26%.

FTIR data for *penta-O-acetyl-β-D-glucopyranoside* (3000–2900 cm^{-1} – (-CH_2,CH bending), 1790 cm^{-1} –(Carbonyl group), 1490 cm^{-1} –(-C-O stretching), 2850-3000 cm^{-1} –(aliphatic C-H Stretching),1350-1480 cm^{-1} –(-C-H Bending)).

The melting point of *penta-O-acetyl-β-D-glucopyranoside* was 125–130°C.

Synthesis of (Hexadecyl-2,3,4,6-Tetra-O-Acetyl-β-D-Glucopyranoside)

Penta-O-acetyl-β-D-glucopyranoside (2.24 mmol) and cetyl alcohol (3.00 mmol) were dissolved in dichloromethane (50.00 ml) and boron trifluoride diethyl etherate (3.50 mmol) was added to it via a syringe. This was stirred under nitrogen atmosphere and the system was sealed. After that, the reaction mixture was stirred at 0°C for 2 h and allowed to slowly warm to ambient temperature. Formation of product was monitored by thin layer chromatography. The reaction mixture was diluted with chloroform (150.0 ml) and washed with saturated sodium bicarbonate solution (50.00 ml) followed by two portions of deionized water. Then, the organic layer was separated and dried over anhydrous sodium sulfate, filtered, and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with hexane and ethyl acetate as (3:1) eluent. The solid product was obtained with a yield of 49.06%.M.p 277-281 °C

FTIR data for *hexadecyl-2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside* 1350-1480 cm^{-1} –(-C-H bending), 1790 cm^{-1} –(carbonyl), 1460 cm^{-1} –(-C-O stretching), 1225 cm^{-1} –(-C-H stretching), 1110 cm^{-1} –(-C-C bending), 1050-1250 cm^{-1} –(C-O stretching)).

Deacetylation of Hexadecyl-2,3,4,6-Tetra-O-Acetyl-β-D-Glucopyranoside

The crude *hexadecyl-2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside* (10.0 mg) was added to a 100 ml round bottom flask. Sodium methoxide in methanol (15.00 ml) was added and purged with nitrogen gas, and stirred in a closed environment for 6 hours. The excess solvents were removed under reduced pressure. The final product was obtained with the yield of 69.59% by series of recrystallization with acetone. M.p 279–285 °C

FTIR data for *hexadecyl-β-D-glucopyranoside* (3600-3400 cm^{-1} –(-OH group), 2900 – 2850 cm^{-1} –(aliphatic a symmetric -C-H stretching), 900 cm^{-1} –(out of plane -C-H bending),1350–1480 cm^{-1} –(Aliphatic -C-H Stretching), 1350-1480 cm^{-1} –(-C-H Bending), 1790 cm^{-1} –(carbonyl group)).

Detailed characterization of *hexadecyl-β-D- glucopyranoside* was carried out by H^1-NMR.

^{1}H NMR (300 MHz, D_2O): δ/ppm 0.88 (t, 3H, H-16'), 1.24–1.30 (m, 26H, 13×CH2, H-3' to H15'), 1.57 (m, 2H, H-2'), 3.48 (dt, 1H, H-1'a), 3.89 (dt, 1H, H-1'b), 3.93 (t, 1H, H-5), 4.16 (d, 2H, H-6a and H-6b), 4.48 (d, 1H, H-1), 5.03 (dd, 1H, H-3), 5.18 (dd, 1H, H-2), 5.38 (dd, 1H, H-4).

Thermotropic and Lyotropic Liquid Crystaline Properties

Thermotropic liquid crystalline properties of *hexadecyl-β-D- glucopyranoside* was observed by polarized light microscope after heating to isotropic phase and while cooling down to room temperature. Lyotropic liquid crystaline properties of the final product, *hexadecyl-β-D- glucopyranoside,* was observed under polarized light microscope by using different polar and non-polar solvents such as, acetone, dichloromethane, ethyl acetate, methanol, ethanol and water with different concentration (Table 1). Optical Microscopic images were taken for the deacetylated final product, *hexadecyl-β-D-glucopyranoside*.

Measurement of CMC

(a) UV- Absorption Spectroscopy
An aqueous stock solution (0.025 mol dm^{-3}) of *hexadecyl-β-D-glucopyranoside* was prepared. Saturated aqueous solution of iodine (2.50 ml) was placed in

Table 1. Concentrations of the prepared lyotropic liquid crystal samples with different solvents

Sample Name	Concentration (%wt)
LW_1	70.69
LW_2	55.71
LW_3	65.82
LW_4	72.59
LW_5	46.00
LW_6	39.13
LM	68.35
LE	69.20
LEA	72.19
LA	70.40

stoppered calibrated centrifuged tubes (15 ml). Varying amounts from the stock solution of *hexadecyl-β-D-glucopyranoside* were added to each falcon tube and the final volume was made up to 10.00 ml by adding distilled water so as to make a series of standard solutions in the concentration range of $(0.250 - 6.00) \times 10^{-5}$mol dm^{-3} [9]. The absorbance spectrum of each solution was measured at 298 K. The absorbance at selected wavelengths of maximum absorbance 351.2 nm and 288.6 nm were recorded and used in the calculation.

(b) Turbidity measurements
From the prepared stock solution of *hexadecyl-β-D-glucopyranoside* in (a) above, a series of solutions in the concentration range of $(0.250 - 5.00) \times 10^{-5}$mol dm^{-3} was prepared by adding varying amounts from the stock solution and making the final volume up to 10.00 ml with distilled water. Then, turbidity of each solution was measured at 298 K using a digital nephlo-turbidity meter.

Preparation of Unstable Microemulsion Systems

Microemulsion systems consisting of olive oil, water and surfactant (Span 80) were formulated at room temperature and 70°C. The ingredients were thoroughly mixed at 2500 rpm in an emulsifier until they appeared to be homogeneous. Morphologies were observed soon after preparation, after 1 hour, two hours, one day and two weeks of preparation. Ternary phase diagrams were constructed based on the morphologies of emulsions observed two weeks after preparation (Fig. 1). Three compositions of macro emulsions and phase separated unstable emulsions were selected from the phase diagram constructed at 70°C (Fig. 1(b)), and newly synthesized compound was introduced (Table 2). The physical stability was assessed by observing morphology of emulsions and thermodynamic stability was determined as described below. The optimum amounts of *hexadecyl-β-D-glucopyranoside* necessary for converting macro emulsions and phase separated unstable emulsions to microemulsions were determined.

Assessment of Thermodynamic Stability of Microemulsions. Microemulsions formed by addition of *hexadecyl-β-D-glucopyranoside* were subjected to the following thermodynamic stability tests.

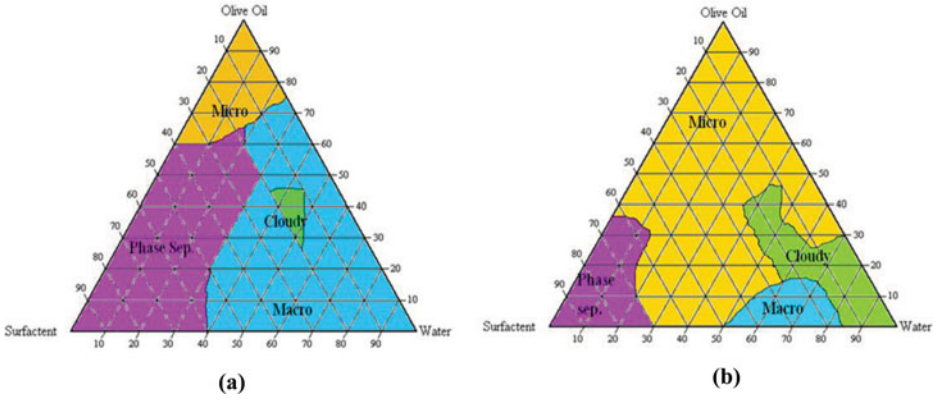

Figure 1. Phase diagram constructed for the emulsion system (a) at Room temperature (b) at 70°C.

Table 2. Compositions of unstable change to macroemulsion systems and stabilized change to microemulsions with LLC

	Mass of each component ± 0.0001/g				Ratio				
Emulsion number	Olive oil	span 80	LLC	Water	Oil	Span 80	Water	LLC	Morphology
E- MA	1.200	3.000	——	7.800	9.95	25	65	——	Macro
E-MB	0.600	2.400	——	9.000	4.95	20	75	——	Macro
E-MC	3.600	2.400	——	6.000	29.95	20	50	——	Macro
E-MALC	1.194	3.000	0.006	7.800	9.95	25	65	0.05	Micro
E-MBLC	0.594	2.400	0.006	9.000	4.95	20	75	0.05	Micro
E-MCLC	3.594	2.400	0.006	6.000	29.95	20	50	0.05	Micro

Centrifuge Stress Test. Microemulsion systems were centrifuged at 6,000 rpm for 30 min and then examined for phase separation [10].

Freeze–Thaw Cycle Stress Test. Microemulsions were subjected to a total of three complete freeze–thaw cycles, each cycle consisting of 24 h at 25°C followed by 24 h at −5°C [11].

Characterization of Microemulsions

Conductivity Measurements

In order to assess both the microemulsion type and stability, conductivity measurements were performed using a conductivity meter. The measurements were performed in triplicate. All measurements were performed immediately after preparation and 14 days after storage at room temperature

Refractive Index

The refractive indices of microemulsion formulations were determined using a refractometer.

Results and Discussion

In order to obtain a maximum β glycoside, the reaction was carried out at 0°C. The β-configuration of purified *hexadecyl-β-D-glucopyranoside* was confirmed by ^{1}H NMR. In the deacetylation step of *hexadecyl-2,3,4,6-tetra-O-acetyl-β-D- glucopyranoside,* stirring time was increased up to 48 hours. This resulted in a significant increase in the final yield of *hexadecyl-β-D-glucopyranoside*.

Study of the Lyotropic and Thermotropic Liquid Crystalline Properties of hexadecyl-β-D-glucopyranoside

After linking the D-glucose moiety and the lipophilic part (hexadecane) through a glycosyl linkage, the molecule becomes amphiphilic comprising a hydrophilic head group and hydrophobic hydrocarbon chain. Therefore sequences of hydrophilic and lipophilic layers are formed due to these microscopic separations. These generated layers have showed the same geometry as the *Smectic A* phase. The 'micro-phase separation' and the 'Closest Packing' are the two basic concepts which correspond to the mesophase behavior of the liquid crystal. If the molecule is a simple-shaped mesogenic compound, there is a high possibility to form a 'Closest Packing' structure because, rod-like molecules tends to pack in an ordered way (liquid crystal phase) rather than in a random way (isotropic phase) [23].

Anisotropic shape of the molecule is the major factor which stabilizes thermotropic LC mesophases. The molecules are self-organized to form thermotropic LC mesophases as a function of temperature. The different texture patterns were observed under the polarized light microscope while changing the temperature (thermotropic liquid crystalline properties; Fig. 2) and with different solvent types and the concentrations (lyotropic liquid crystalline properties; Fig. 3). Molecules have high rotational and translational entropy above their melting points and also convert into isotropic state.

Upon heating the *hexadecyl-β-D-glucopyranoside* to isotropic liquid and cooling back to room temperature, fan-like texture pattern was observed (Fig. 4a) under crossed polarizers

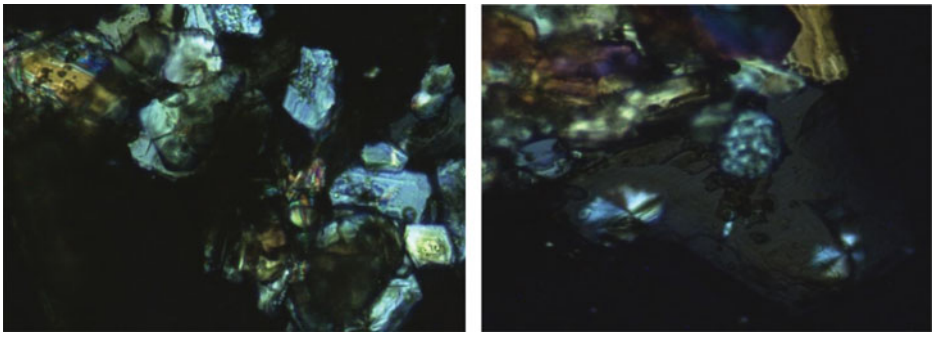

Figure 2. Thermotropic LC textures for deacetylated product. Magnification 400; crossed.

in a polarized light microscope with water as the solvent at lower concentration (Table 1). The Periodic stripe domains appeared on the fan like texture at high concentrations (Table 1) of deacetylated compound, while increasing the concentration 55.71% wt to 72.59% wt (Fig. 4b and 4c). As the amount of the solvent increased, the Periodic stripe domains were broadened (Fig. 4d and 4e). This effect may be due to loosely packing arrangements low concentration of the compound. The molecules which contain long alkyl chains tend to organize in a hexagonal pattern. According to the XRD data for the compound in the water matrix, a single intense peak can be found in the small angle region, at $2\theta = 2.60^\circ$ with a d-spacing of 34.20 A$^\circ$ (Fig. 5a). An intense peak and two smaller peaks (three reflection peaks) can be seen in the small angle region ($2\theta = 2^\circ$-10°,) which is a required observation for columnar hexagonal phases [24,25]. Thus, it can be concluded that the compound shows columnar hexagonal phases with water as the solvent. Also the molecular length calculated from Gaussian modelling (a simple molecular modelling package), was around 25.094 A$^\circ$ and the d-spacing is greater than 1 and less than 2 times the molecular length. Therefore, molecules may exist in bilayers forming a head-to-head molecular packing in two dimensions (Fig. 6a) [24,25].

Similarly, upon cooling, small fan like texture pattern Characteristic for Smectic A phase was observed with methanol and ethanol (Fig. 3b–3c). According to the XRD data for the compound in the ethanol matrix, a single intense peak can be found in the small angle region, at $2\theta = 2.81^\circ$ with a d-spacing of 31.58 A$^\circ$ (Fig. 5b) which is characteristic for smectic phases. Here also the calculated from Gaussian modelling (a simple molecular modelling package), molecular length was around 25.094 A$^\circ$ and the d-spacing is greater than 1 and less than 2 times the molecular length. Therefore, molecules may exist in bilayers forming a head-to-head molecular packing in two dimensions (Fig. 6b) [24,25].

However, this compound also showed typical Schlieren texture patterns with non-polar solvents such as acetone and ethyl acetate. In ethyl acetate, a characteristic "threading" texture pattern was observed throughout the colored regions, corresponding to molecular domains which are aligned with one of the optical polarizers (Fig. 3d, e) at 42°C to room temperature. Even this texture contains thread like structure; it also exhibits two- and four-fold brushes. Smectic Schlieren textures exhibit only four-fold brushes, and therefore, this texture may be related to the typical behavior for nematics or smectic (Fig. 3d). In the corresponding XRD data for the compound in the ethyl acetate matrix intense peak was observed at $2\theta = 3.24^\circ$ in the small angle region (Fig. 5c) corresponding to d-spacing of 27.21 A$^\circ$. This value is almost similar to the calculated molecular length, 25.094 A$^\circ$ at its most stable conformation in the model. Therefore it can be concluded that molecules may

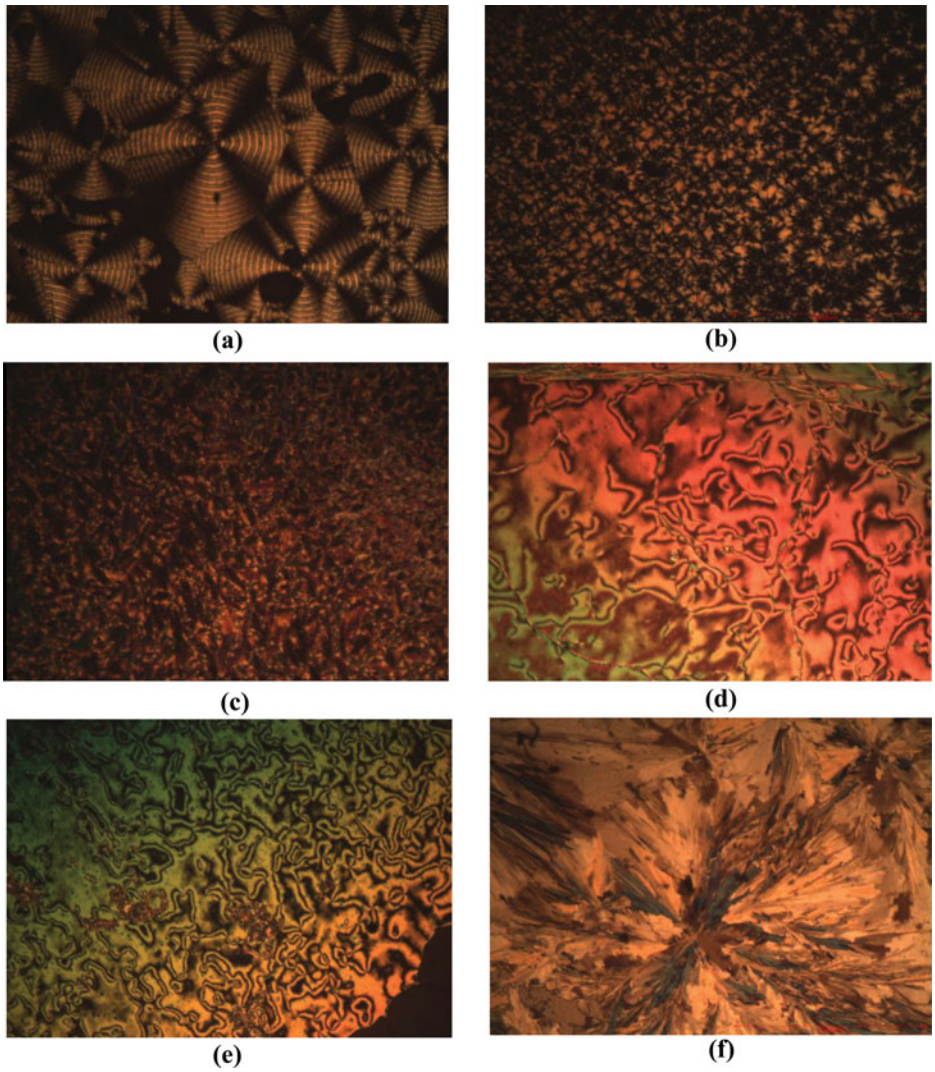

Figure 3. Lyotropic LC textures for deacetylated product with (a) water (LW_1), (b) methanol (LM), (c) ethanol (LE), (d) ethyl acetate (LEA), (e) acetone (LA), (f) after evaporation of water: Magnification 400; crossed. Concentrations–Table 1

exist in monolayer with loosely packed Smectic arrangement because the molecules which contain long alkyl chains, tend to organize in the layers in a loosely packed arrangement to form smectic phases (Fig. 6c) [24,25].

Spherulite texture of the crystalline phase was observed after evaporation of water.

Measurement of CMC

Depending on the concentration of the amphiphiles, proportion of molecules present at the surface or as micelles in the bulk of the solvent is changed. At low concentration, molecules

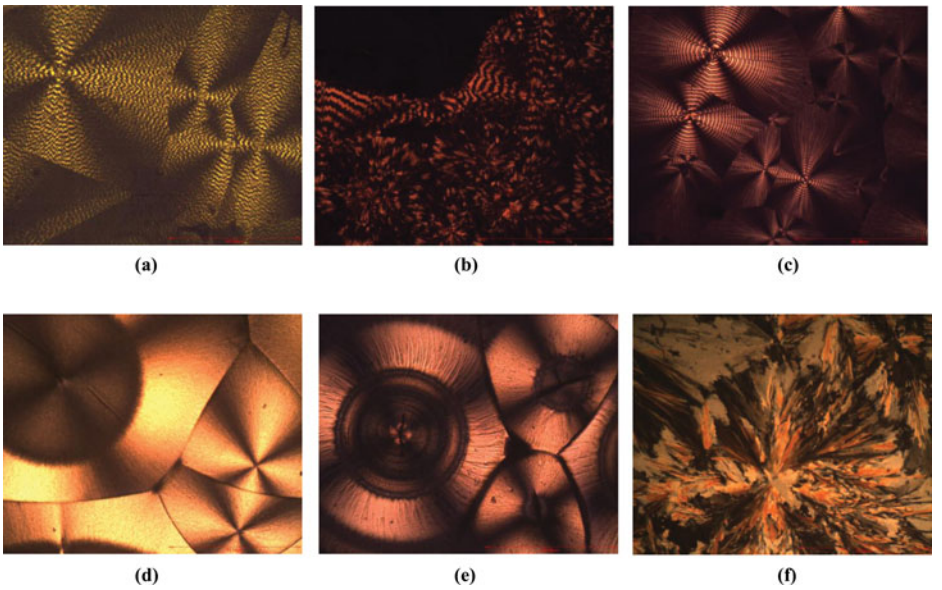

Figure 4. Lyotropic LC textures for deacetylated product with water; (a) low concentration (LW_2), (b) and (c) High concentration (LW_3, LW_4), (d) and (e) higher dilution regions (LW_5, LW_6), (f) after evaporation of water: Magnification 400; crossed. Concentrations–Table 1

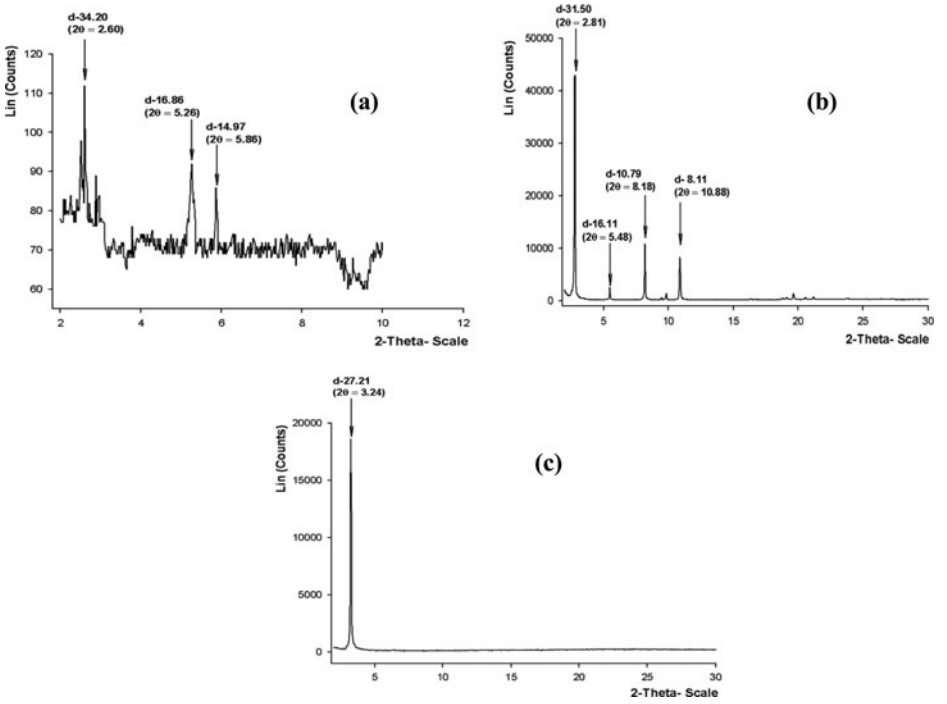

Figure 5. XRD patterns for lyotropic liquid crystal with different solvents; (a) water, (b) ethanol, (c) ethyl acetate: Step time 4 s at 25°C.

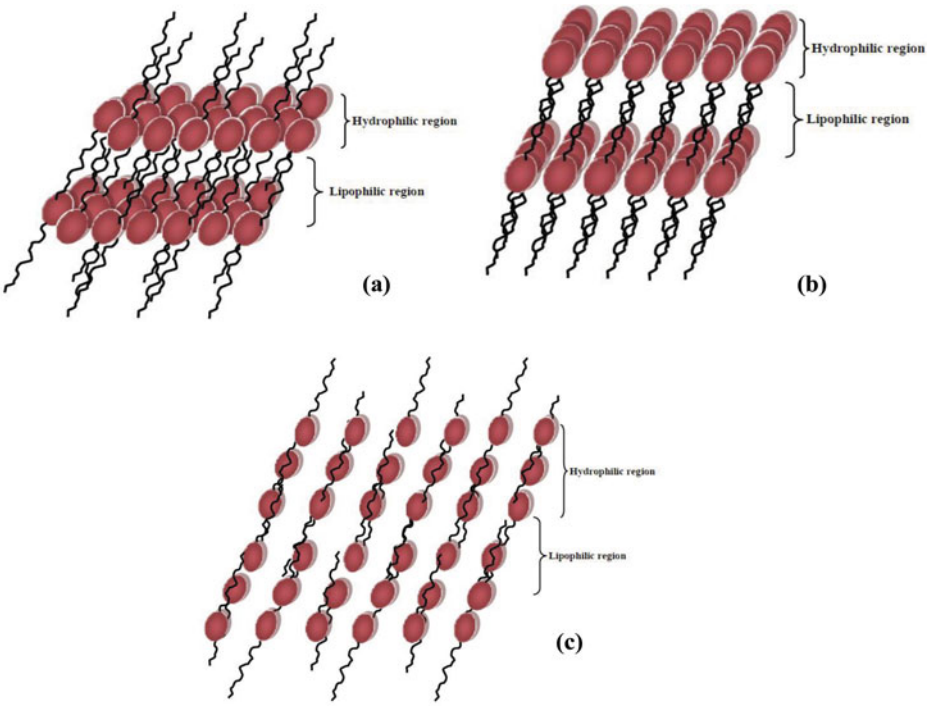

Figure 6. Molecular packing with different solvents (a) water, (b) ethanol, (c) ethyl acetate.

tend to arrange on the surface. At higher concentration levels the surface becomes crowded and excess molecules will arrange into micelles. At a critical concentration of surfactant the solvent surface becomes completely loaded such that any further tiny additions undergo spontaneous self-association into ordered structures called micelles. That concentration is called the Critical Micelle Concentration (CMC). This is an important fundamental property which affects most of bulk physical properties.

Usually to determine CMC of surfactants some physicochemical parameters such as conductometry, tensiometry, fluorescence emission spectroscopy, calorimetry, kinetic approaches, light scattering, NMR spectroscopy and cyclic voltametry are used [13–19].

CMC of *hexadecyl-β-D-glucopyranoside* was studied using two different methods.

(a) *UV-Visible Spectrometric Studies*

The UV-Visible spectrophotometric studies were conducted to determine the CMC of the synthesized glucoside using donor-acceptor complex formation of Iodine-surfactant molecules. Due to formation of donor-acceptor complex, the spectral absorbance at maximum absorbance wave length (λ_{max}) is reduced. The formation of the complex is mainly due to the fact that nonionic surfactants have the ability to perform as iodophores or I_2 carriers without destroying the surfactant properties [9]. Saturated I_2 solutions absorb at 351.2 nm and 288.6 nm. Figure 7 shows the plot of absorbance Vs concentration of glucoside at 351.2 nm and 288.6 nm. It shows sharp distinct break point at 1.55×10^{-5}mol dm^{-3} and 1.53×10^{-5} mol dm^{-3} for 288.6 nm and 351.2 nm respectively.

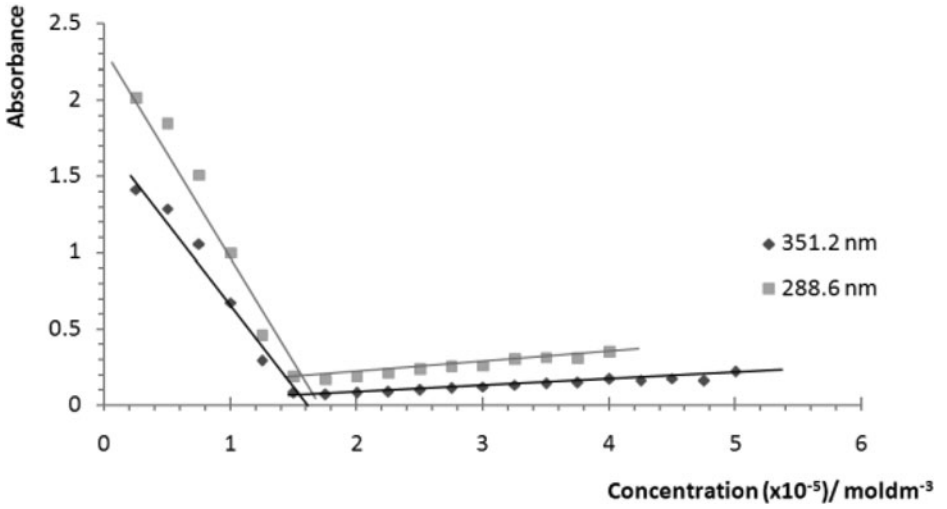

Figure 7. Absorbance Vs Concentration plot at two maximum absorbance wave lengths, concentration related to the distinct break point is the CMC value at 27°C.

(b) Turbidity Measurements

The intensities of a transmitted and diffused monochromatic light at 90° by the solution are measured and its ratio in Nephlo turbidity units (NTU) is taken as the turbidity. The turbidity changes with concentration in such a way that the change before and after the critical point results in a break point which is the CMC [17,18].

The prepared series of aqueous solutions of surfactant with concentration in the range of $(0.25 - 5.0) \times 10^{-5}$mol dm^{-3}, shows significant turbidity in the measurable linear range of the instrument. A plot of turbidity Vs concentration (Fig. 8) showed a distinct break point at 0.98×10^{-5}mol dm^{-3} in the plot which corresponds to the CMC value. The CMC

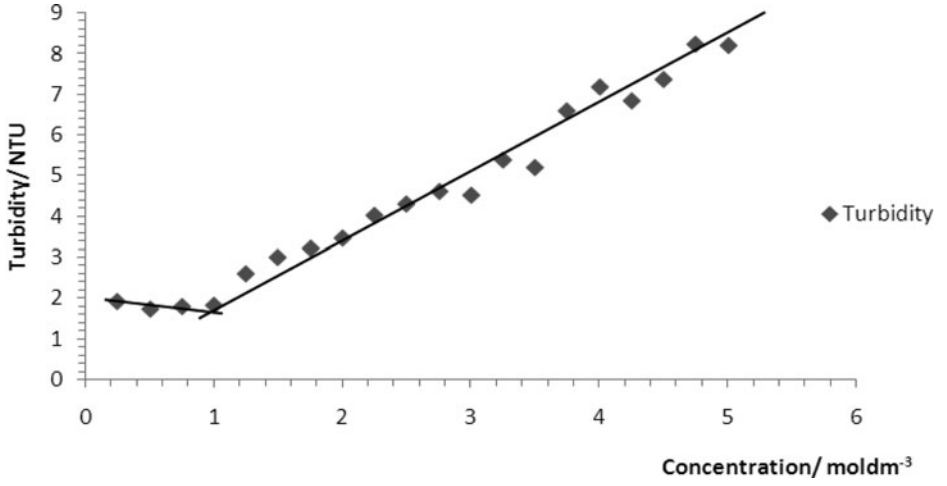

Figure 8. Turbidity Vs concentration of surfactant solution, concentration corresponding to the distinct break point is the CMC value at 27°C.

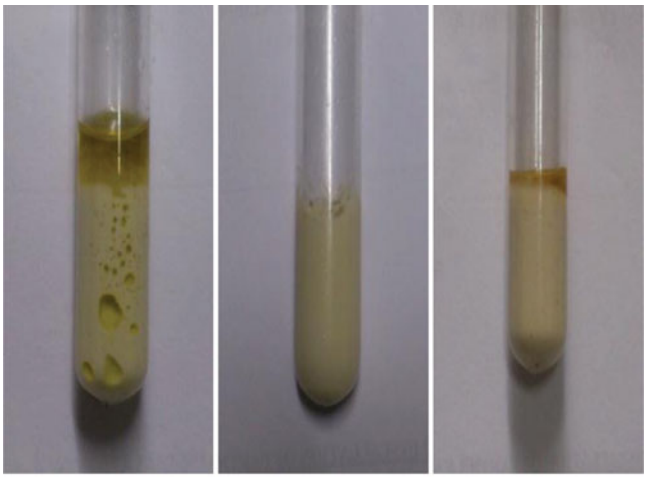

Figure 9. Unstable Emulsion system (a) E-MA, (b) E-MB, (c) E-MC without adding LLC

value thus obtained from turbidity measurement is slightly lower than that obtained from the UV method (1.55×10^{-5}mol dm^{-3}) but they are in the same order.

The HLB value of the surfactant provides an idea about the lowest interfacial tension between oil phase and water phase. It indicates several physicochemical parameters and behaviors of the surfactant. The HLB value of synthesized glycolipid, *hexadecyl-β-D-glucopyranoside* calculated using Equation (1), was 8.86. This HLB value suggests that the synthesized glycolipid is suitable for making self-emulsifying oils and as a water in oil emulsifier.

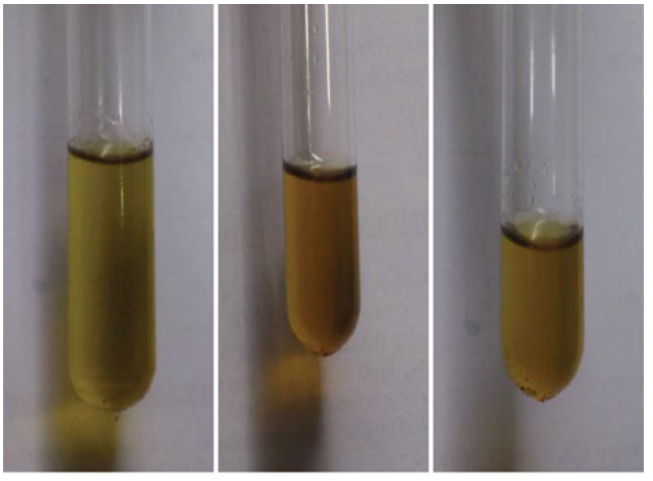

Figure 10. Microemulsion system (a) E-MALC, (b) E-MBLC, (c) E-MCLC with LLC

Table 3. Parameters for the selected microemulsion systems

Emulsion number	Conductivity($\times 10^{-6}$)/ S	pH value	Refractive index
E-MALC	1.753	6.9	1.4610
E-MBLC	1.718	7.2	1.4590
E-MCLC	1.723	7.2	1.4640

Construction of Ternary Phase Diagrams

A phase diagram for a particular binary or ternary system depicts the relationship among the phase components of the system and the phase behavior of the formulation. Since the free energy requirement for the formation of the emulsion system is very small, therefore, the morphologies at stable states should be observed very carefully [24]. In this study, olive oil was selected as the oil phase and Span 80 was chosen as the surfactant (S). Two separate pseudo ternary phase diagrams were constructed for the same system of oil, water and Span 80 at room temperature and 70°C. Figure 1(a) is the ternary phase diagram for emulsions formulated at room temperature. It clearly shows four types of emulsions; microemulsions, macro emulsions, phase-separated emulsions and cloudy emulsions. On heating to 70°C (Fig. 1(b)), the microemulsion region was expanded significantly narrowing phase-separated and macro emulsion regions.

Stabilization of Unstable Emulsion Systems with LLC

The compositions of macro emulsions and unstable emulsions with phase separation selected for our study are shown in Table 2. Upon inclusion of glycolipid, *hexadecyl-β-D-glucopyranoside* (LLC) to the unstable macro emulsion systems a distinct change to microemulsions was observed (Figs. 9, 10).

By introducing minimum amount of 0.05 wt% of newly synthesized LLC material, *hexadecyl-β-D-glucopyranoside,* as a co-surfactant, unstable macro emulsions were successfully converted to transparent micro emulsions and the stability was increased. Morphologies were observed through naked eye.

Characterization of Microemulsion Systems

In order to characterize the selected stabilized microemulsion systems given in Table 2, pH values, refractive indices and conductivity measurements were carried out. Table 3 summarizes the measured parameters. The refractive index values of the three stabilized emulsions were 1.46. The observed refractive index value of 1.46 for all three stabilized microemulsions is in the range expected for transparent isotropic systems [25].

The conductivity values of the stabilized microemulsions are in the range of $(1.753–1.718) \times 10^{-6}$ S. Generally, all formulations are low viscous and the measurements were performed in triplicate. All measurements were performed after 14 days storage at room temperature.

Conclusion

Carbohydrate lyotropic liquid crystal, *hexadecyl-β-D-glucopyranoside* was synthesized with a maximum yield of 63.47%. The chemical structure, surfactant and liquid crystal properties were confirmed.

Upon heating the *hexadecyl-β-D-glucopyranoside* to isotropic temperature and cooling back to room temperature, fan-like texture pattern was observed. The inherent rods like shape of the molecules favor arrangement as hexagonal array. As observed from XRD data molecules may exist in bilayers forming a head-to-head molecular packing in two dimensions. Similarly, upon cooling, small fan like texture pattern characteristic for Smectic A phase was observed with methanol and ethanol. Here also XRD data suggested that molecules may exist in bilayers forming a head-to-head molecular packing in two dimensions.

However, this compound also showed typical Schlieren texture patterns with non-polar solvents such as acetone and ethyl acetate. In ethyl acetate, a characteristic "threading" texture pattern was observed throughout the colored regions, corresponding to molecular domains which are aligned with one of the optical polarizers. Even this texture contains thread like structure; it also exhibits two- and four-fold brushes. Smectic Schlieren textures exhibit only four-fold brushes, and therefore, this texture relates to smectic phase because XRD data concluded that molecules may exist in monolayer, molecules with loosely packed Smectic arrangement in the packing because the molecules which contain long alkyl chains, tend to organize in loosely packed layers so that form smectic phases.

The CMC for *hexadecyl-β-D-glucopyranoside* from both UV visible spectroscopic method and turbidity method was in the region between 10^{-5}–10^{-4}mol dm^{-3} which is typical for nonionic surfactants. Calculated HLB value 8.86 indicates that synthesized glycolipid is suitable for making self emulsifying oils and water in oil emulsions. *Hexadecyl-β-D-glucopyranoside* has the ability to transform macro emulsions and unstable emulsions to microemulsions. By introducing only 0.05 wt% of LLC-*hexadecyl-β-D-glucopyranoside* the conversion is affected to produce stable microemulsions. The results strongly suggest that the synthesized glycolipid is suitable for use as co-surfactant to stabilize the microemulsions.

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