

ELECTRONIC SUPPLEMENTARY MATERIAL (ESI)

Facile solvent free synthesis of polymerised sucrose functionalised polyoxyethylene (23) lauryl ether by microwave irradiation

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Materials and Methods

Polyoxyethylene (23) lauryl ether or Brij^R35 [C₁₂H₂₅(OCH₂CH₂)₂₃OH, MW 1198.8], sucrose (C₁₂H₂₂O₁₁, MW 342.3), potassium peroxydisulphate, isopropyl alcohol were procured from S.D Fine Chemicals, Mumbai, India. All the chemicals were of A.R grade and were used as received.

Synthesis of surfactant (1)

As a typical procedure for the preparation of the surfactant (1), sucrose and polyoxyethylene (23) lauryl ether (weight of sucrose 10.2 g, 85.14% w/w for polyoxyethylene (23) lauryl ether; molar ratio of sucrose to polyoxyethylene (23) lauryl ether; 1: 0.33) was irradiated under microwave (Start-R, Milestone, Italy) for 300 s in presence of KPS (0.015 g or 0.0023 mol/L). The yellowish gummy product thus obtained was isolated by precipitating in isopropyl alcohol (IPA) (1:2.25 w/v). The product was separated and purified by re-precipitating in IPA. Finally the product was dried under reduced pressure and stored in nitrogen environment. Yield: 8.8 g

The amount of sucrose and polyoxyethylene (23) lauryl ether was optimized to get a stable gummy product. Other compositions used in terms of one mole equivalent of sucrose to polyoxyethylene (23) lauryl ether were 0.11, 0.22, 0.44, 0.54 and 0.7. For the first three cases, viscous solutions were obtained but there was no gummy material upon precipitation in IPA and for the last two, these products were liquid in nature. [KPS] used for all the reactions was 0.0023 mol/L.

The reaction was also carried out repeating the above process in absence of KPS in order to rule out the possibility of forming product in absence of it. Formation of microscopically heterogeneous product (2) upon cooling and precipitation in IPA was observed (vide infra SEM images).

Scanning Electron Microscope

The scanning electron micrographs of the samples were recorded on a Carl-Zeiss Leo VP 1430 instrument by applying 15 kV accelerating voltage. The samples were dispersed in acetone and vacuum dried on an aluminum stub.

NMR

¹H and ¹³C NMR spectra of the samples were recorded at ambient conditions in D₂O using d₆-DMSO as internal standard (for ¹³C) on a Bruker Ultrashield 500 MHz spectrometer.

Thermal analysis

Differential scanning calorimetric (DSC) measurements were carried out on a Mettler Toledo DSC 822^e system taking approximately 7.7 mg material in an closed aluminum pan weighing 15 mg and the measurements were done using a temperature programme of -50–250 °C at 2 °C min⁻¹ in two cycles heating as well as cooling under nitrogen atmosphere, empty closed aluminum pans were used as reference. TGA was carried

out on a Mettler Toledo TGA/SDTA 851^e system taking approximately 3 mg material in an open aluminum pan using the temperature programme of 40–500 °C at heating rate of 10 °C min⁻¹ in air atmosphere.

UV-Vis spectrometry

UV-Vis spectra were recorded on a Varian CARY 500 Scan UV-Vis-NIR spectrophotometer at 25 °C using water as blank.

Surface tension measurements

The surface tension at 27.0 °C was measured by the static Wilhelmy plate using dynamic contact angle tensiometer (DCAT 21, Data physics, Germany). To ensure removal of surface-active contaminants, all glassware in contact with the sample were cleaned in chromic acid and rinsed with double distilled water. Experiments were carried out in triplicate

Fluorescence measurements

Steady-state fluorescence measurements were performed on air-equilibrated solutions using a Perkin-Elmer Luminescence spectrometer LS-50B. Pyrene was excited at 334 nm and the detection wavelengths were $I_1 = I_M = 373$, $I_3 = 384$ nm, $I_E = 475$ nm. Excitation and emission slits were 2.0/2.0 nm, respectively. The solutions containing the probe were prepared by transferring a sufficient amount of a methanol stock solution of pyrene to the solution of Brij 35 and the surfactant (1). The final pyrene concentration used for the measurements was 1.80×10^{-6} mol/L corresponding to an absorbance 0.029 at 334 nm. For quenching experiments, cetyl pyridinium chloride (CPCl, 0.02 to 0.1 %) was used as quencher.

Gel permeation chromatography (GPC)

The molecular weights and molecular weight distributions (M_w/M_n) of the surfactant (1) was measured on a Waters-Alliance 2695 GPC system using Waters ultra hydrogel 500 column, MPower 2 Software was used for the analyses. The solvent used was 0.1 M NaNO₃ with flow rate 0.1 ml/min. Standard graphs were prepared using dextran standards.

HPLC and ESI-MS

HPLC studies were conducted on a Shimadzu instrument (Shimadzu Corporation, Japan) comprising Rheodyne injector, 250 mm x 4.6mm (i.d.) Nucleosil C18 stainless steel column (5 μm particle size, 300 Å pore size) (Sigma-Aldrich, Inc, USA), 6AD pumps, SPD-10A uv-vis detector and LC-10 chromatography manager. The samples were injected with a 20 μl microsyringe (Hamilton, Reno, Nevada, USA). Isocratic elution was performed at 40 °C with H₂O/Phosphate Buffer (pH= 6.5) (7:3, v/v) mobile phase at a constant flow rate of 1.0 mL min⁻¹. UV detection was carried out at 254 nm. For mass spectrometry, a Waters Q-ToF micro YA-260 instrument equipped with electro spray ionization interface, Micromass mass selective detector and Waters Mass Lynx software (version 4.0) was used.

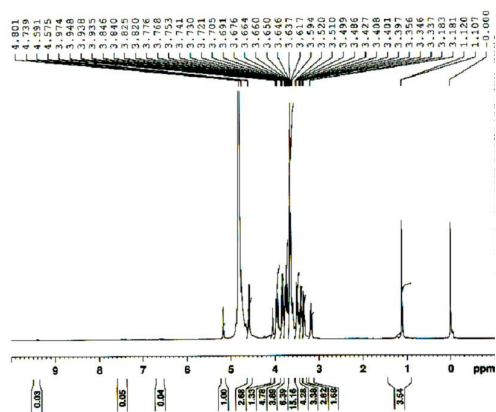


Fig. S1: ¹H spectra of surfactant (1)

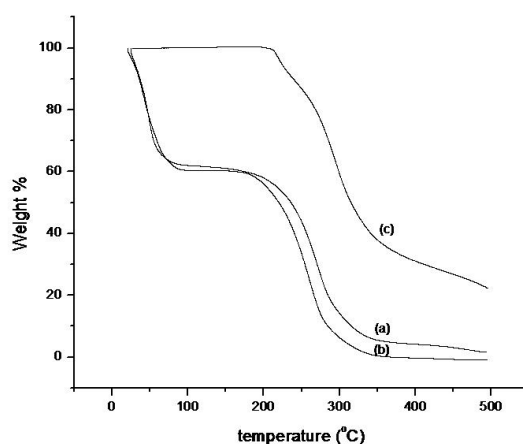


Fig. S4: TGA thermogram (a) surfactant (1) (b) pure polyoxyethylene (23) lauryl ether (c) sucrose.

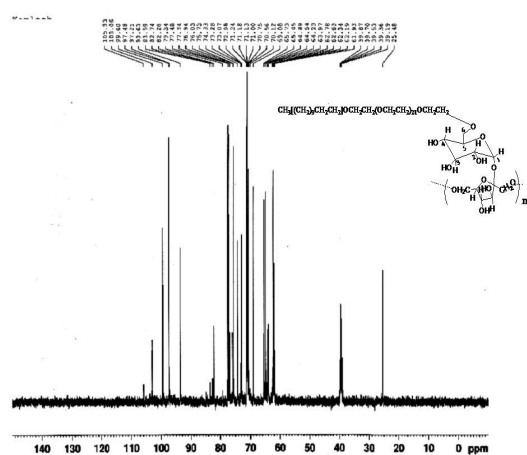


Fig. S2: ¹³C spectra of surfactant (1)

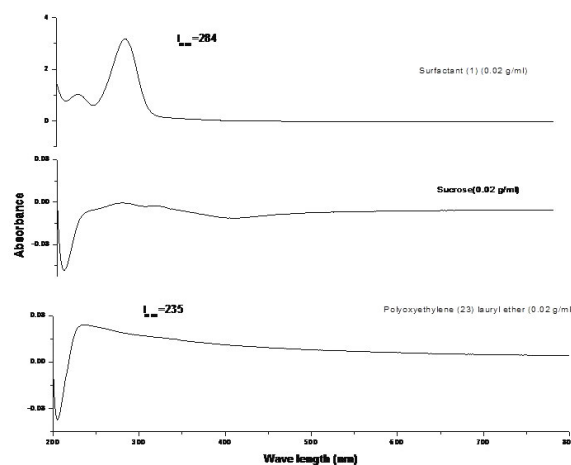


Fig. S5: UV-Vis spectra of surfactant (1), pure polyoxyethylene (23) lauryl ether and aqueous solution of sucrose.

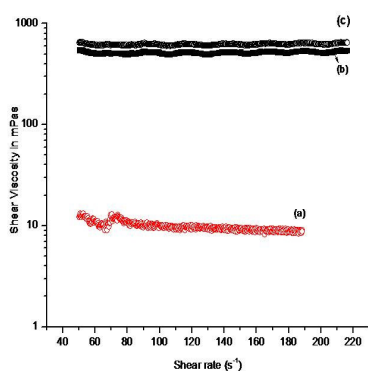


Fig. S3: Shear viscosity of (a) polyoxyethylene (23) lauryl ether (b) Product (2) and (c) Surfactant (1).

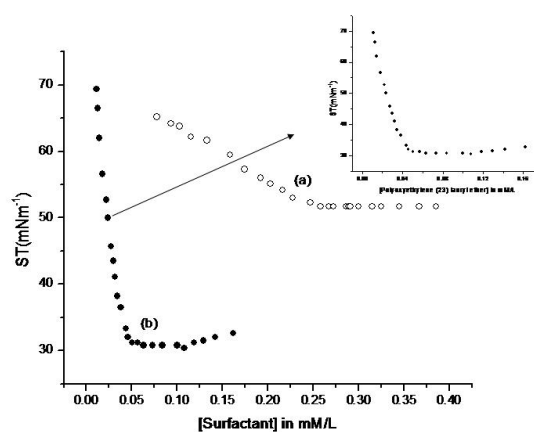


Fig. S6: Surface tension measurement for (a) surfactant (1) (b) pure polyoxyethylene (23) lauryl ether.

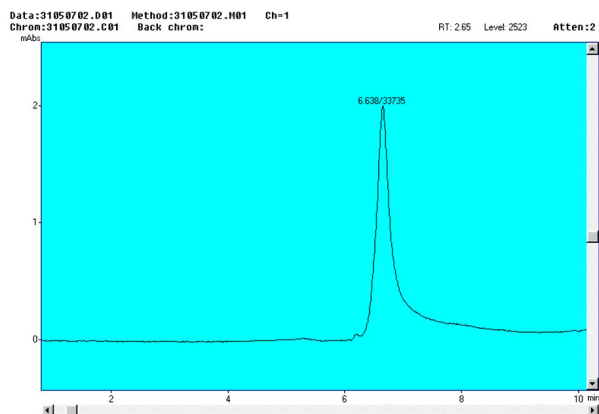


Fig S 14 : LC for the surfactant when molar ratio sucrose to polyethylene (23) lauryl ether was 1: 0.33

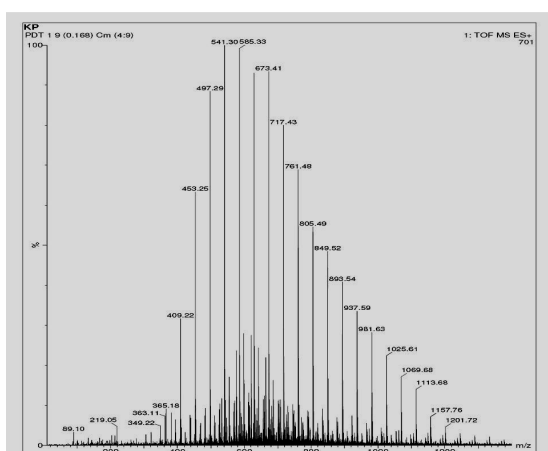


Fig S 15 : ESI-MS the surfactant when molar ratio sucrose to polyethylene (23) lauryl ether was 1: 0.33

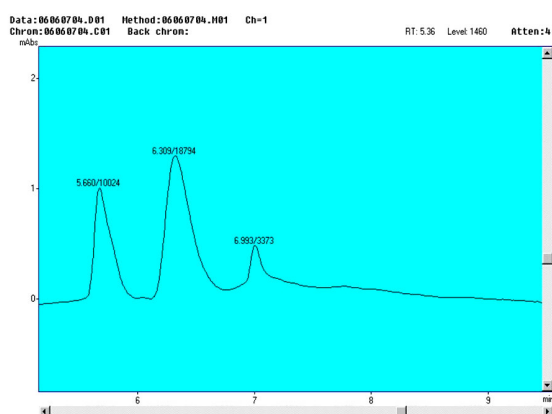


Fig S 16 : ESI-MS the surfactant when molar ratio sucrose to polyethylene (23) lauryl ether was 1: 0.11

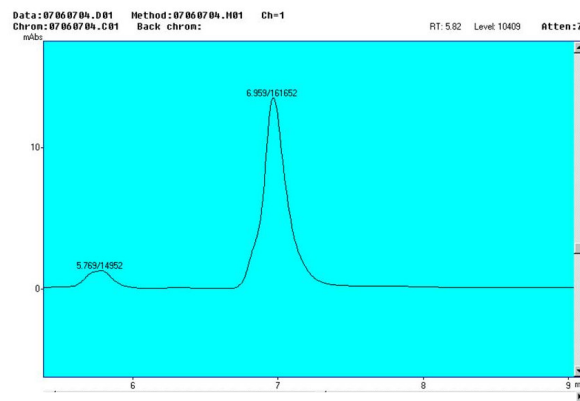


Fig S 17 : ESI-MS the surfactant when molar ratio sucrose to polyethylene (23) lauryl ether was 1: 0.22

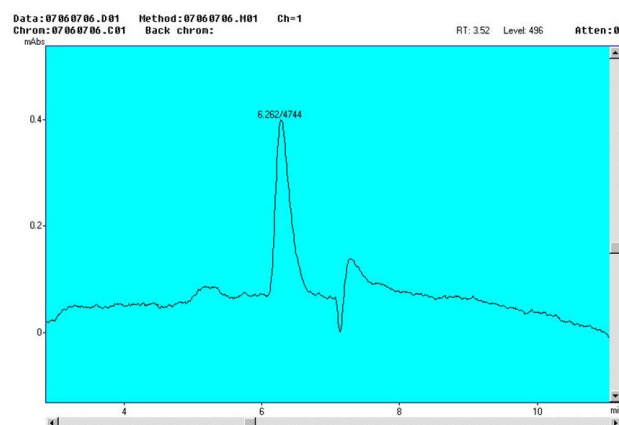


Fig S 18 : LC for the surfactant when molar ratio sucrose to polyethylene (23) lauryl ether was 1: 0.44

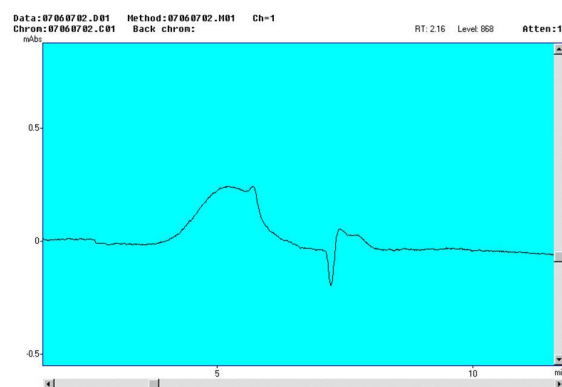


Fig S 19 : LC for the surfactant when molar ratio sucrose to polyethylene (23) lauryl ether was 1: 0.54