Electronic Supplementary Information

A Class of Surfactants *via* PEG Modification of the Oleate Moiety of Lactonic Sophorolipids: Synthesis, Characterisation and Application

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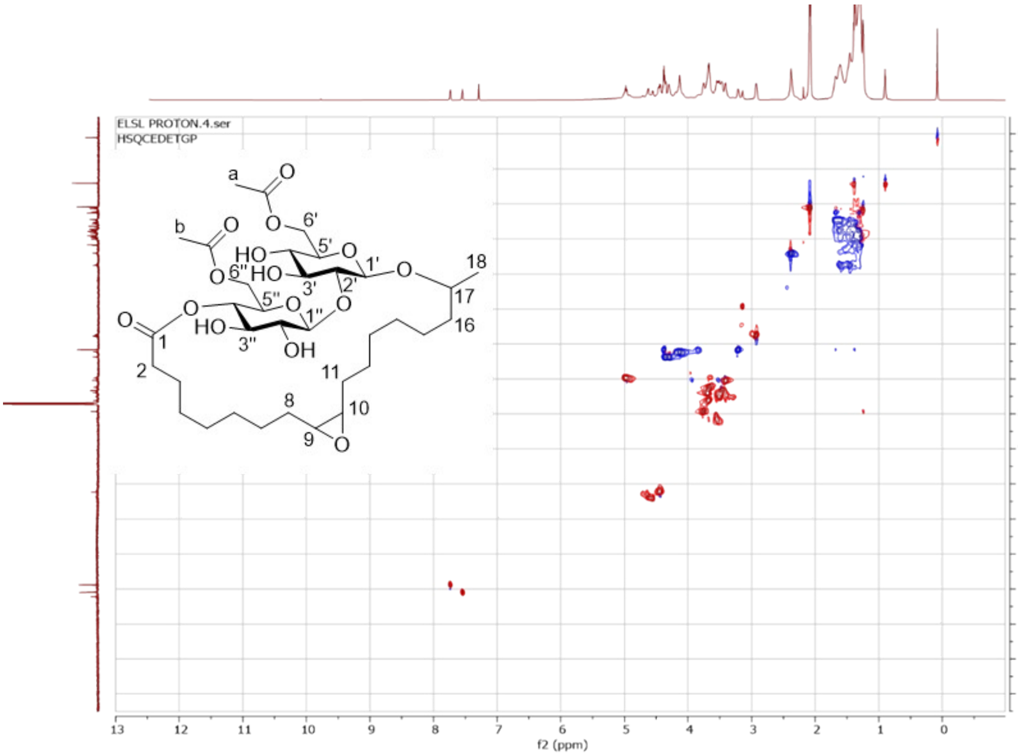
1.0 2D NMR Assignment for Introduction

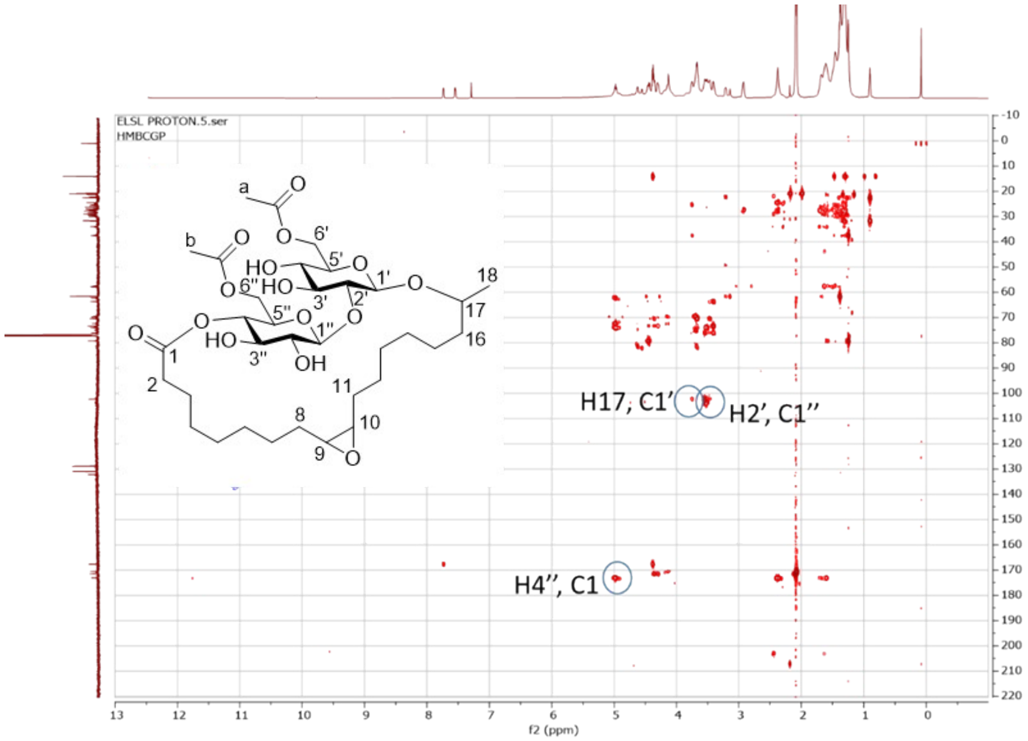
1.1 Heteronuclear Single Quantum Coherence (HSQC) Spectrum for Epoxidised Lactonic Sophorolipid (ELSL)



18	0.9 ppm
Others	1.40 ppm
a,b	2.08 ppm
2	2.38 ppm
9, 10	2.93 ppm
4’, 2’, 2”, 5”	3.50 ppm
17, 3’, 3”, 5’	3.72 ppm
6’	4.17 ppm
6”, 6”, 6’	4.40 ppm
1’, 1”	4.59 ppm
4”	4.98 ppm

Figure S 1: Heteronuclear Single Quantum Coherence Spectrum for epoxidised lactonic sophorolipid confirming that the glycosidic bonds at C17 bonded to C1’, C4’’ bonded to C1 and between C1’’ and C2’’ were retained despite the acidic medium in which the reaction took place.

1.2 Heteronuclear Multiple Bond Correlation (HMBC) for Epoxidised Lactonic Sophorolipid (ELSL)



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4”	4.98 ppm

Figure S 2 :Heteronuclear Multiple Bond Correlation Spectrum for epoxidised lactonic sophorolipid confirming that the glycosidic bonds at C17 bonded to C1’, C4’’ bonded to C1 and between C1’’ and C2’’ were retained despite the acidic medium in which the reaction took place.

1.3 Heteronuclear Multiple Bond Correlation (HMBC) for Epoxidised Lactonic Sophorolipid ring-opened with PEG 400 (PLSL 400)

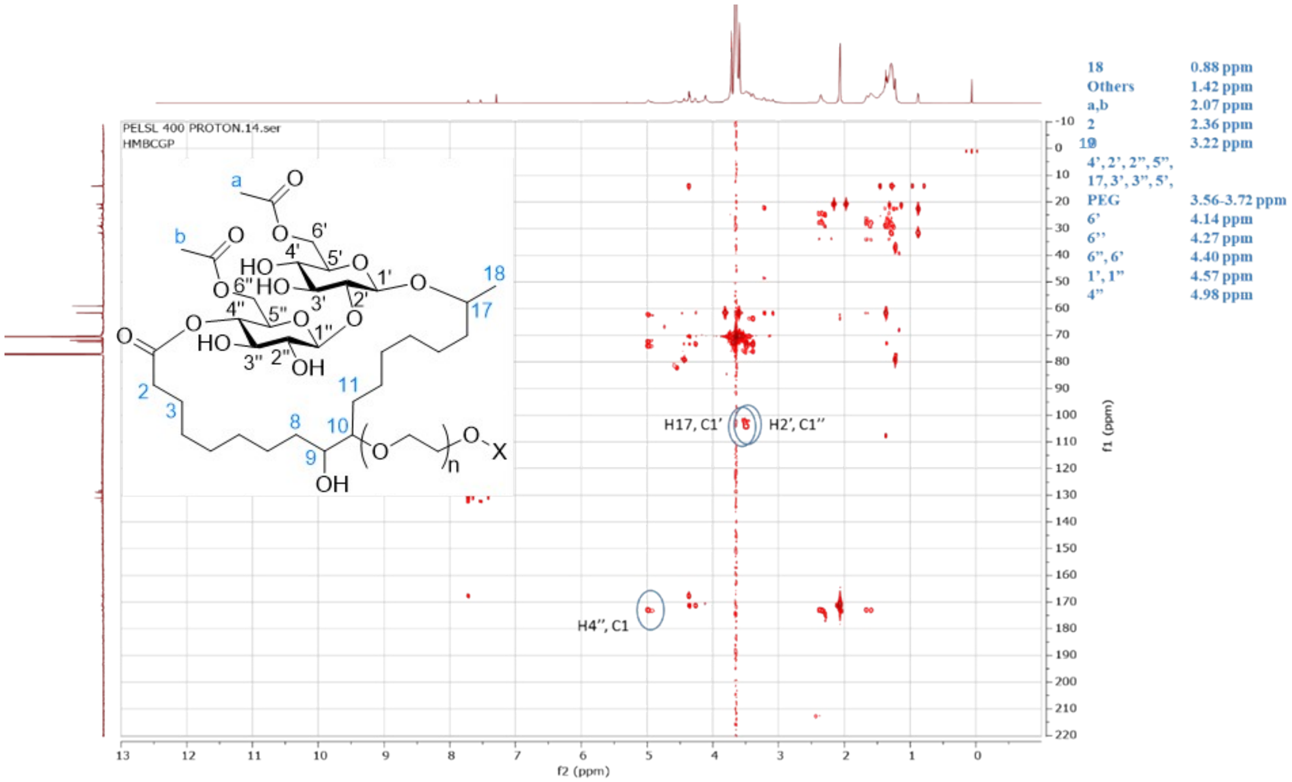
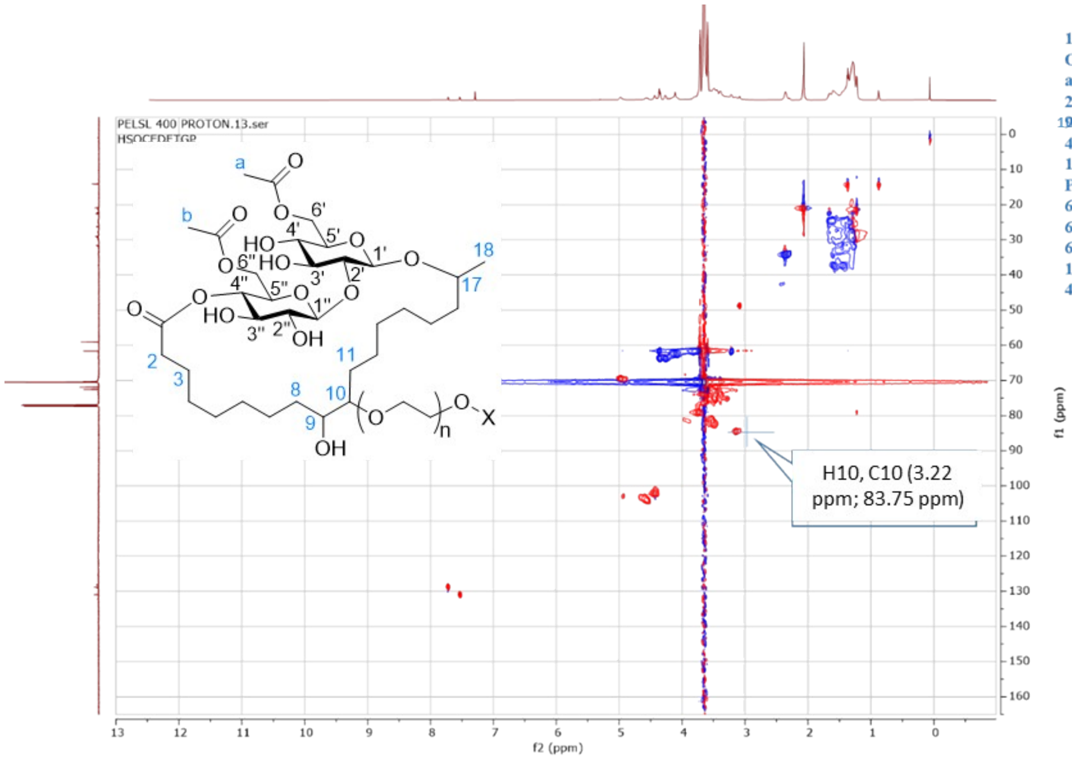


Figure S 3: Heteronuclear Multiple Bond Correlation Spectrum for PEGylated lactonic sophorolipid from PEG400 confirming that the glycosidic bonds at C17 bonded to C1', C4'' bonded to C1 and between C1'' and C2'' remained intact after ring-opening reaction.

1.4 Heteronuclear Single Quantum Correlation Spectrum (HSQC) for Epoxidised Lactonic Sophorolipid ring-opened with PEG 400 (PLSL 400)



H10, C10 (3.22 ppm; 83.75 ppm)

18	0.88 ppm
Others	1.42 ppm
a,b	2.07 ppm
2	2.36 ppm
10	3.22 ppm
4’, 2’, 2”, 5”, 17, 3’, 3”, 5’, PEG	3.56-3.72 ppm
6’	4.14 ppm
6’’	4.27 ppm
6”, 6’	4.40 ppm
1’, 1”	4.57 ppm
4”	4.98 ppm

Figure S 4: Heteronuclear Single Quantum Correlation Spectrum for PEGylated lactonic sophorolipid from PEG400 confirming that the PEG chain was attached to position 10 of the hydrophobic chain of the sophorolipid.

2.0 HLB Calculation for Synthesised Surfactants

For HLB calculation involving surfactants with capped PEGs, the methyl group at the PEG end was included in the hydrophobic group as shown in Figure S 5.

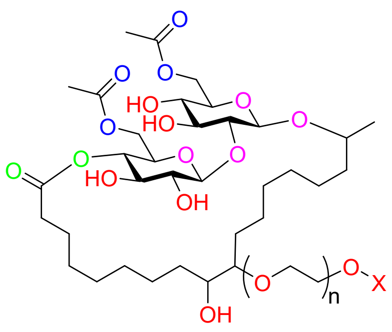


Figure S 5: Hydrophilic groups identified in sophorolipid-based surfactants for HLB calculation (ethers and hydroxyls in red; acetals in purple; lactone ester in green and acetate esters in blue).

For PLSL 400, HLB was calculated using equation 1 as:

$$\mathrm{HLB} = \frac{\text{mass of PEG400} + \text{mass of OHs} + \text{mass of ether groups} + \text{mass of ester groups}}{\text{Molecular weight of surfactant}} \mathrm{x} 20$$

$$= \frac{414 + 85 + 132 + 64}{1135} \mathrm{x}\ 20$$

$$= 12.25$$

Therefore, HLB for PEG 400 was 12.25

HLB for other surfactants was calculated the same way and listed in the Table S1

Table S1 HLB values and average molecular weight obtained for sophorolipid-based surfactants

Surfactant code	*Surfactant description*	*HLB*	*Av. MW*
ELSL	Epoxidised lactonic sophorolipid	7.95	704
PLSL400	Epoxidised lactonic sophorolipid ring opened with PEG 400	12.25	1135
MPLSL400	Epoxidised lactonic sophorolipid ring opened with MePEG 400	12.06	1149
MPLSL750	Epoxidised lactonic sophorolipid ring opened with MePEG 750	13.75	1457
PLSL1000	Epoxidised lactonic sophorolipid ring opened with PEG 1000	14.89	1721
PLSL1500	Epoxidised lactonic sophorolipid ring opened with PEG 1500	16.09	2249

3.0 Model Reactions

3.1 Reaction of Methyl Oleate Epoxide with Triethylene Glycol

15 mmol triethylene glycol (TEG) was heated to 80 °C in a glass vial and $Yb(TFA)_3$ (0.5% wt with respect to methyl oleate epoxide) added and stirred rigorously on a multipoint reactor. 1 mmol methyl oleate epoxide (EMO) was added dropwise after which the temperature was raised to 100 °C while stirring rigorously. Progress of reaction was monitored for 1 hour by taking portions at intervals for GC-FID and NMR spectroscopy analyses. ^1H NMR (400 MHz, $CDCl_3$, ∂ ppm): 0.81 (3H, t, $C\mathit{H}_3CH_2$-), 1.22 (26H, overlapped, -$(C\mathit{H}_2)_7HC(OH)CH((OCH_2CH_2)_3\text{-}OH)(C\mathit{H}_2)_6CH_2COOCH_3$), 2.24 (2H, t, -$C\mathit{H}_2COOCH_3$), 3.06 (1H, m, -$HC(OH)C\mathit{H}(OCH_2CH_2)_3\text{-}OH)$-), 3.42 (1H, m, -$\mathit{H}C(OH)$-), 3.63 (20H, m, overlapped, -$HC(OH)CH(OC\mathit{H}_2C\mathit{H}_2)_3\text{-}OH)$-); ^{13}C NMR (100 MHz, $CDCl_3$, ∂ ppm): 14.16, 22.71, 24.97, 25.18, 25.24, 25.38, 25.46, 28.97, 29.07, 29.11, 29.17, 29.26, 29.31, 29.38, 29.48, 29.55, 29.60, 29.71, 29.87, 29.91, 31.46, 31.91, 31.94, 32.72, 32.76, 34.10, 34.14, 51.51, 51.48, 61.54, 61.59, 69.94, 70.37, 70.57, 72.73, 73.15, 73.91, 85.27, 174.36; IR (ATR, ν, cm^{-1}), 3446 (O-H str.), 2924 (s. CH_3 str.), 2856 (s. CH_2 str.), 1737 (C=O str.), 1457 (a. CH_3 bend), 1350 (s. CH_2 bend), 1248 (C-O- str.), 1101 (a. C-O-C str.).

From a 100% EMO conversion, ~80% product having a molecular mass of 464 g/mol was obtained. The chromatogram (Figure S 6) also showed excess TEG, an unknown compound suggested as butylated hydroxyl toluene (BHT) by GC-MS NIST library, saturated fatty esters residual in the epoxide and TEG diol. Interestingly, there appeared no trace of oligomers, including those from the PEG diol reacting twice, in the chromatogram after 35 minutes. IR spectrum showed bands expected in the product: a strong stretch band for C-O-C ether linkage centred at 1100 cm^{-1}, reduced OH band intensity with the disappearance of the epoxy band (817 cm^{-1} symmetrical stretch) from the epoxide as shown in Figure S 7.

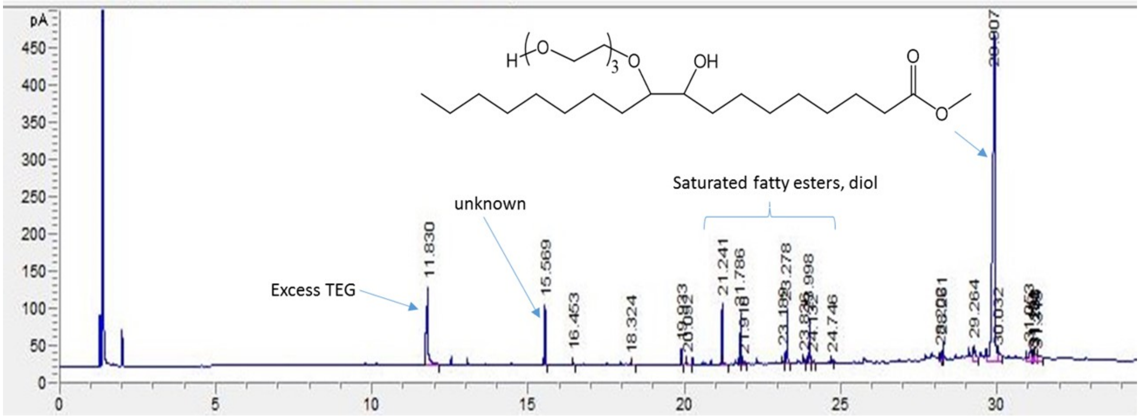


Figure S6 GC-FID chromatogram of ring-opened epoxidised methyl oleate in TEG catalysed by $Yb(TFA)_3$

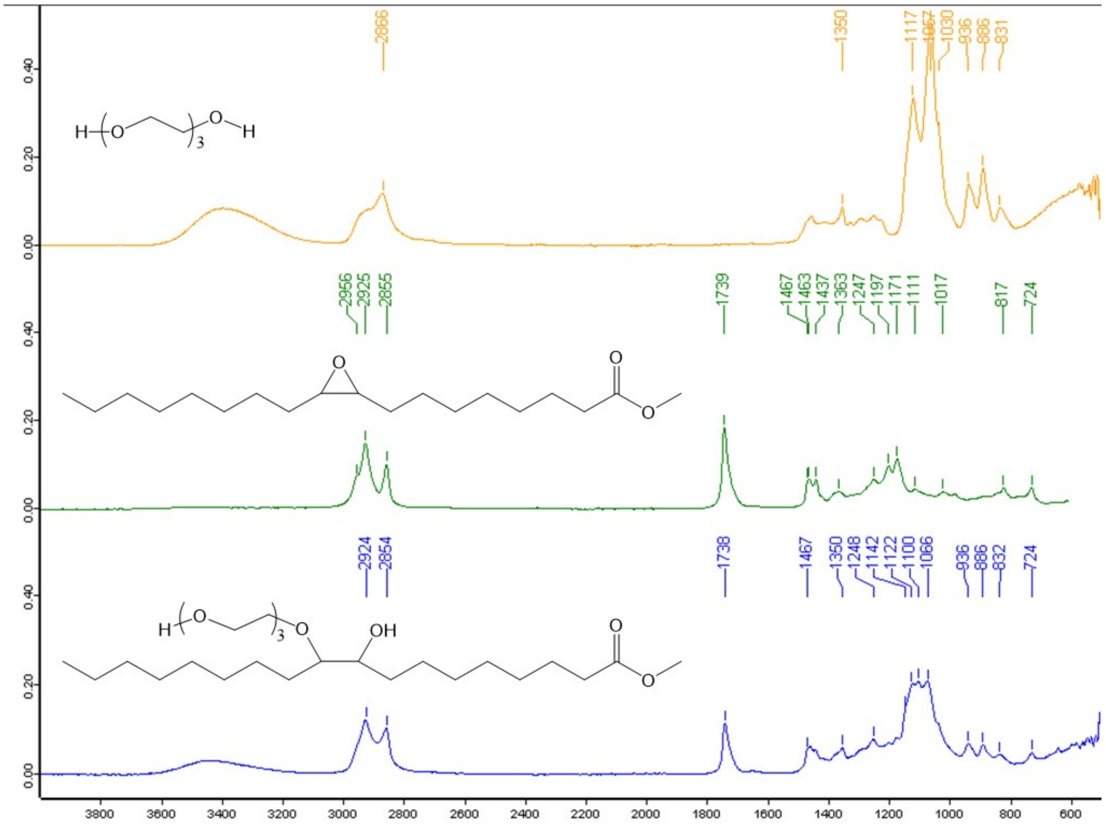


Figure S 7 FT-IR spectra of triethylene glycol, epoxidised methyl oleate and ring-opened epoxidised methyl oleate

^{1}H NMR spectra of reactants and product (Figure S 8) showed total conversion of EMO as the peaks **c** and **d** for epoxy protons at 2.74 ppm from the epoxide disappeared in the product spectrum to reappear now as α-protons of the hydroxyl group **d** at 3.42 ppm and ether group **c** at 3.06 ppm of the ring-opened epoxide. Additionally the epoxy ring β-protons **b** lost its distinct position and moved up-field in the product spectrum. All other peaks in the epoxide retained their relative positions on the chemical shift after ring opening. Overlapping peaks **h** and **e** in the product spectrum showed an integration value of ~21H. Peak **h**, the epoxide ester methyl protons, is 3 H while peak **e** the TEG chain proton is ~18 H instead of 13 H expected. This suggests there is still excess TEG left unremoved. As earlier discovered and stated unreacted TEG and EG were not as effectively removed as PEGs because of decreasing hydrophilicity with decreasing repeating ethoxyl chain.

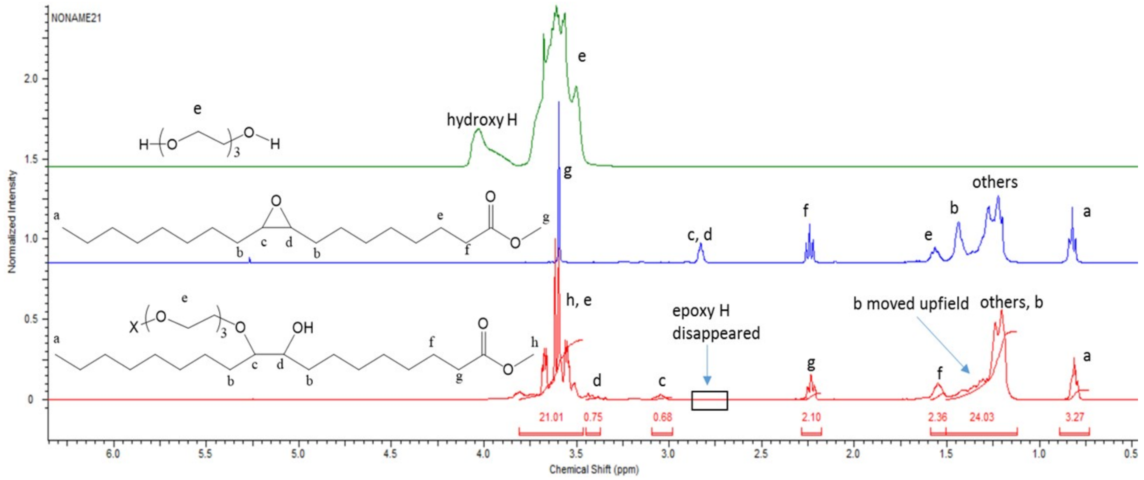


Figure S 8 ^{1}H NMR spectra of triethylene glycol, epoxidised methyl oleate and ring-opened epoxidised methyl oleate

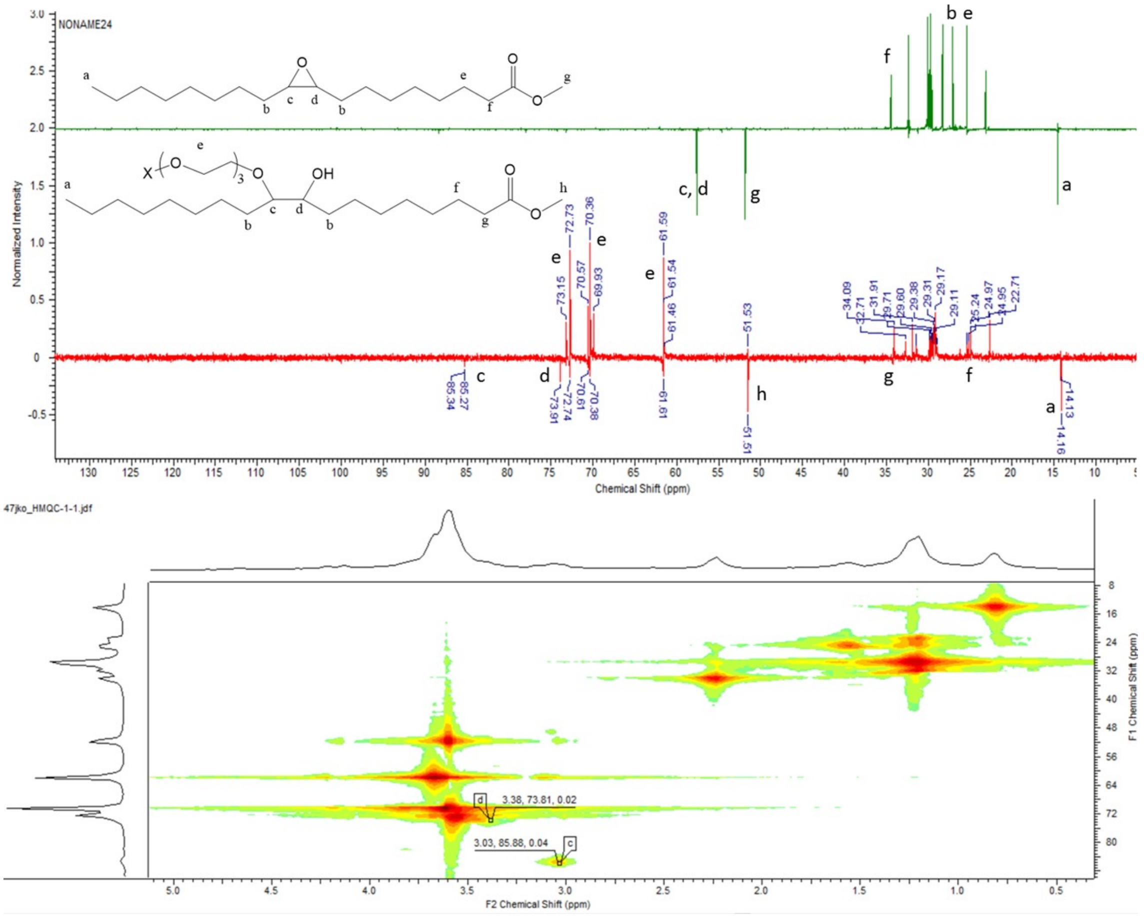


Figure S 9 Carbon DEPT NMR spectra of epoxidised methyl oleate and ring-opened epoxidised methyl oleate. HSQC of ring-opened epoxidised methyl oleate (below).

Carbon DEPT NMR spectra of EMO and product confirmed the total conversion of the epoxide with the loss of epoxy carbons **c** and **d** (57.02 ppm, 57.06 ppm) in the product spectrum (Figure S 9). The new α-carbons for hydroxyl group **d** (73.91 ppm) and ether group **c** (85.27 ppm) of the ring-opened epoxide were confirmed with support from HSQC and HMBC spectra. The loss or displacement of the β-epoxy carbon peaks **b** on the product spectrum was noted which corroborates the observation from the proton NMR spectra.

3.2 Reaction of Methyl Oleate Epoxide with PEG 400

Typically 10 mmol PEG was heated to 80 °C in a 50 mL round bottom flask followed by addition of Fe-mont (5% wt of PEG) and allowed to mix thoroughly for 2 minutes. 5 mmol epoxide was added in drops through a dropping funnel for over 5 to 10 minutes and temperature raised to 100 °C while stirring rigorously with a stopper lightly placed on the flask. Progress of reaction was monitored with ^{1}H NMR spectroscopy with portions taken for analysis. The reaction was stopped after 50 minutes and resulting product transferred into a 250 mL beaker, diluted with 50 mL ethyl acetate and suction filtered to recover the catalyst. Product identification was by IR spectroscopy, ESI mass spectrometry, CHN elemental analysis, DSC, SFC and ^{1}H and proton-decoupled ^{13}C NMR spectroscopy.

^{1}H NMR (400 MHz, CDCl$_3$, ∂ ppm): 0.77 (3H, t, *J*=6.3 Hz, $\mathrm{C\mathit{H}_3CH_2}$-), 1.33 (26H, overlapped, -$\mathrm{(C\mathit{H}_2)_7HC(OH)CH((OCH_2CH_2)_9\text{-}OH)(C\mathit{H}_2)_6CH_2COOCH_3}$), 2.19 (2H, t, -$\mathrm{C\mathit{H}_2COOCH_3}$), 2.99 (1H, m, -$\mathrm{HC(OH)C\mathit{H}((OCH_2CH_2)_9\text{-}OH)}$-), 3.61 (36H, overlapped, -$\mathrm{\mathit{H}C(OH)CH((OC\mathit{H}_2C\mathit{H}_2)_9\text{-}OH)(CH_2)_7COOC\mathit{H}_3}$); ^{13}C NMR (100 MHz, CDCl$_3$, ∂ ppm): 14.12, 22.61, 24.90, 25.38, 25.65, 29.04-299.90, 31.08, 31.89, 33.09, 34.04, 51.45, 61.47, 70.14-70.81, 72.73, 73.33, 84.53, 174.32; ESI-MS accurate mass, 749.5022 (MNa$^+$, 749.5010 calc. for $C_{37}H_{74}NaO_{13}$); CHN: % C (60.673 found, 60.820 calc.), % H (10.089 found, 9.920 calc.), % N (nd); IR (ATR, ν, cm^{-1}), 3468 (O-H str.), 2925 (a. CH$_2$ str.), 2858 (s. CH$_2$ str.), 1739 (C=O str.), 1462 (a. CH$_3$ bend), 1352 (s. CH$_2$ bend), 1250 (C-O- str.), 1102 (a. C-O-C str.).

Accurate mass determination for methyl oleate epoxide ring-opened with PEG 400 (PEMO 400) in the microTOF mode and ESI spectra showed the mass/charge ions binomially distributed across the chain length of the surfactants (Figure S10). With an average molecular weight of 400 gmol^{-1} and EO number 9 for PEG the PEMO 400 has molecular weight of 726 gmol^{-1} but across a distribution of masses 573-837 gmol^{-1}. No molecular mass ions corresponding to PEG400 (423, i.e., 400+ 23 from Na) or methyl oleate epoxide (335, i.e., 312 + 23 from Na) were observed, indicating total conversion of epoxide and the effective removal of excess PEG. Surprisingly, there was still a trace of Adogen 464 used as a PTC in epoxidation reaction left in the PEMO 400 surfactant. Additionally, we could not confirm any clear presence of disubstitution of the epoxide onto the diol (reaction of the diol at both ends), this would have given a broad polymodal distribution around 1126 gmol^{-1} but was not observed in our analysis, though further investigation would be required to fully discount the possibility.

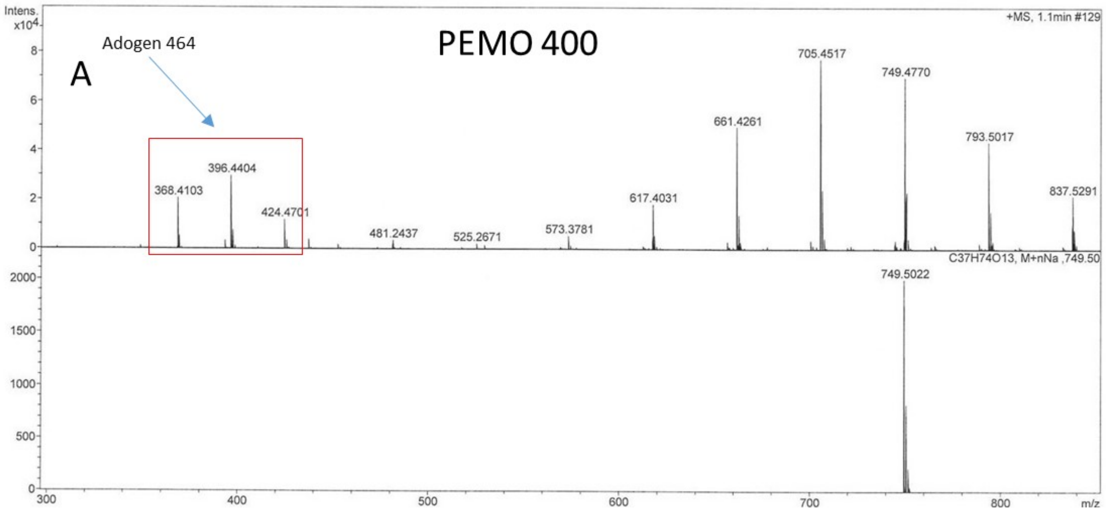
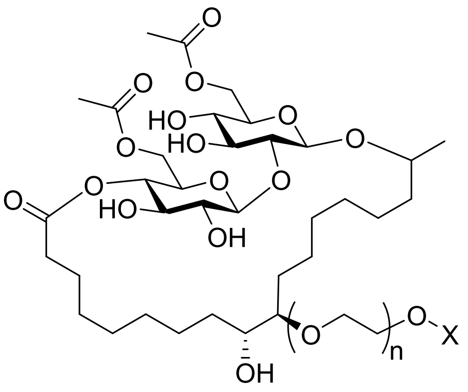
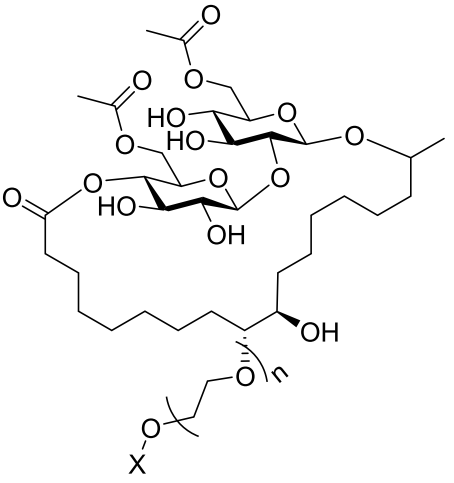
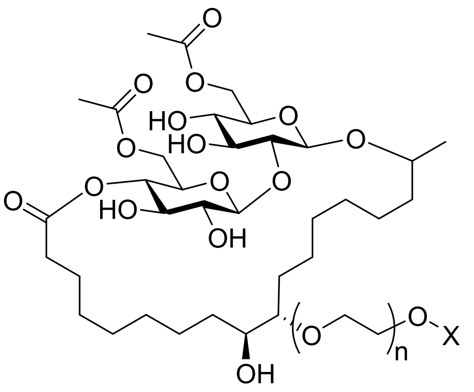


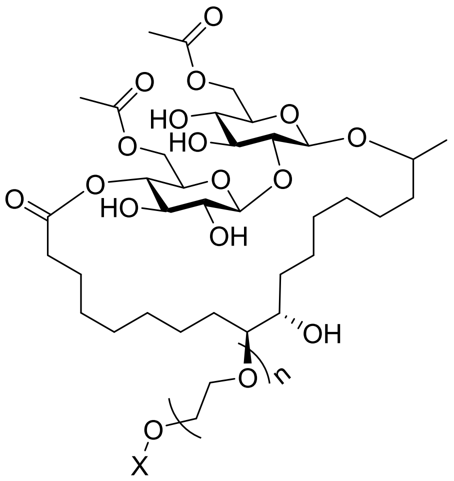
Figure S10 ESI spectrum of alkyl oleate surfactant based on PEG 400. PEMO 400 surfactant with a trace impurity of Adogen 464 residue from epoxidation process.

4.0 Regio and Stereo structures of the surfactant

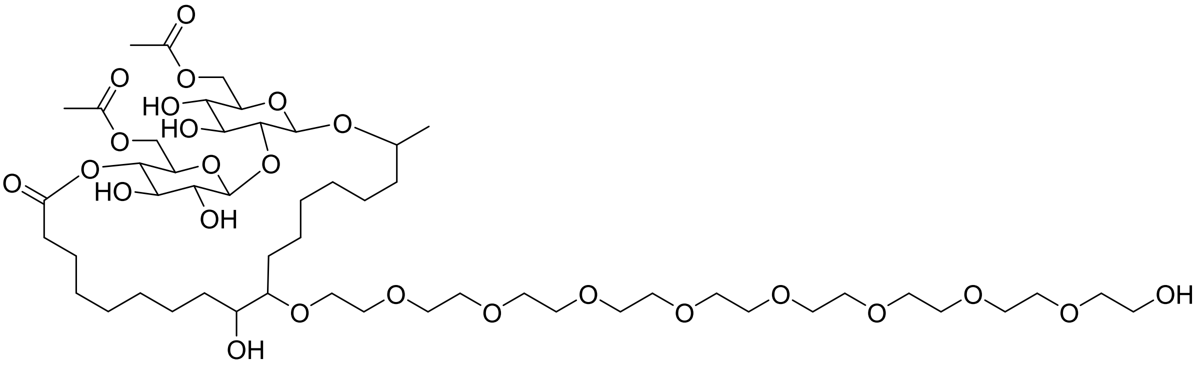




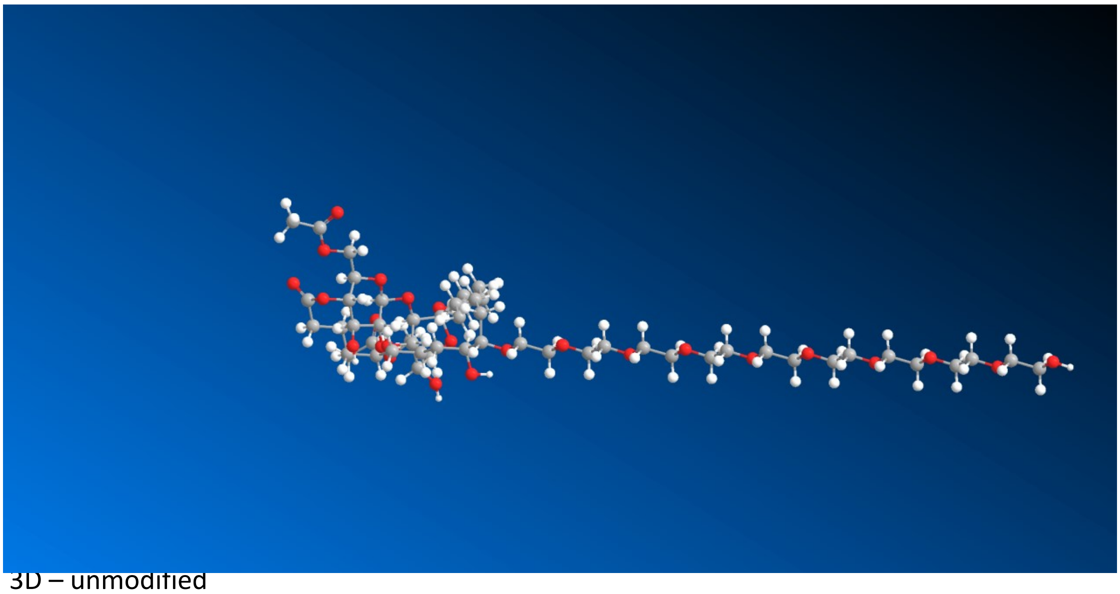




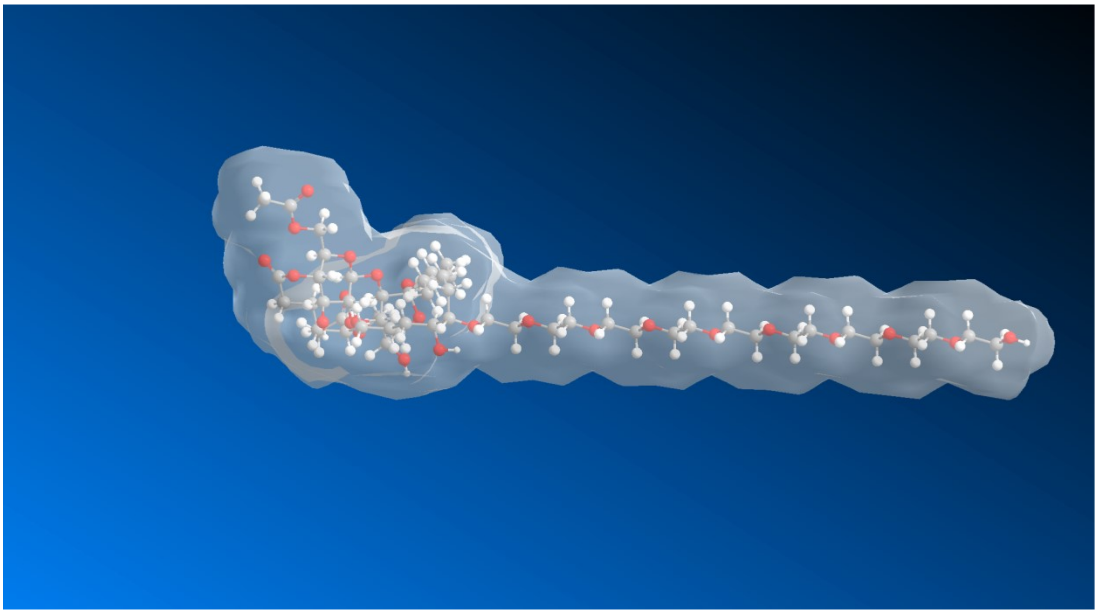
5.0 3D models of Sophorolipid ring-opened with PEG 400 (PLSL 400)



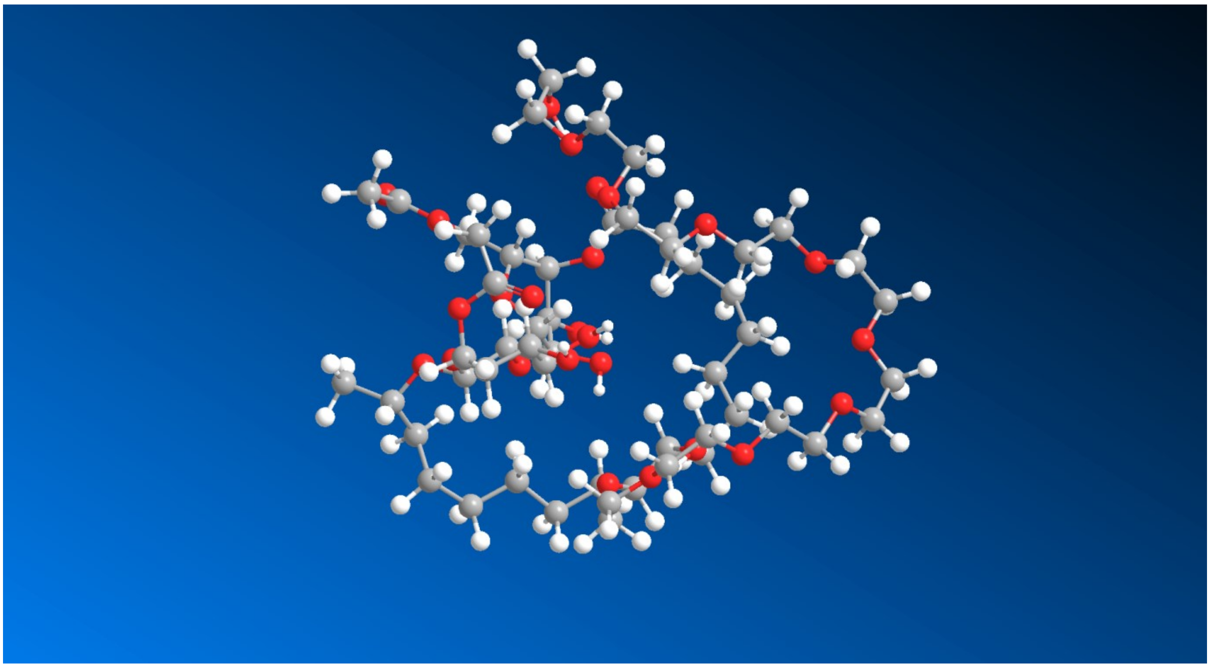
Chemdraw structure



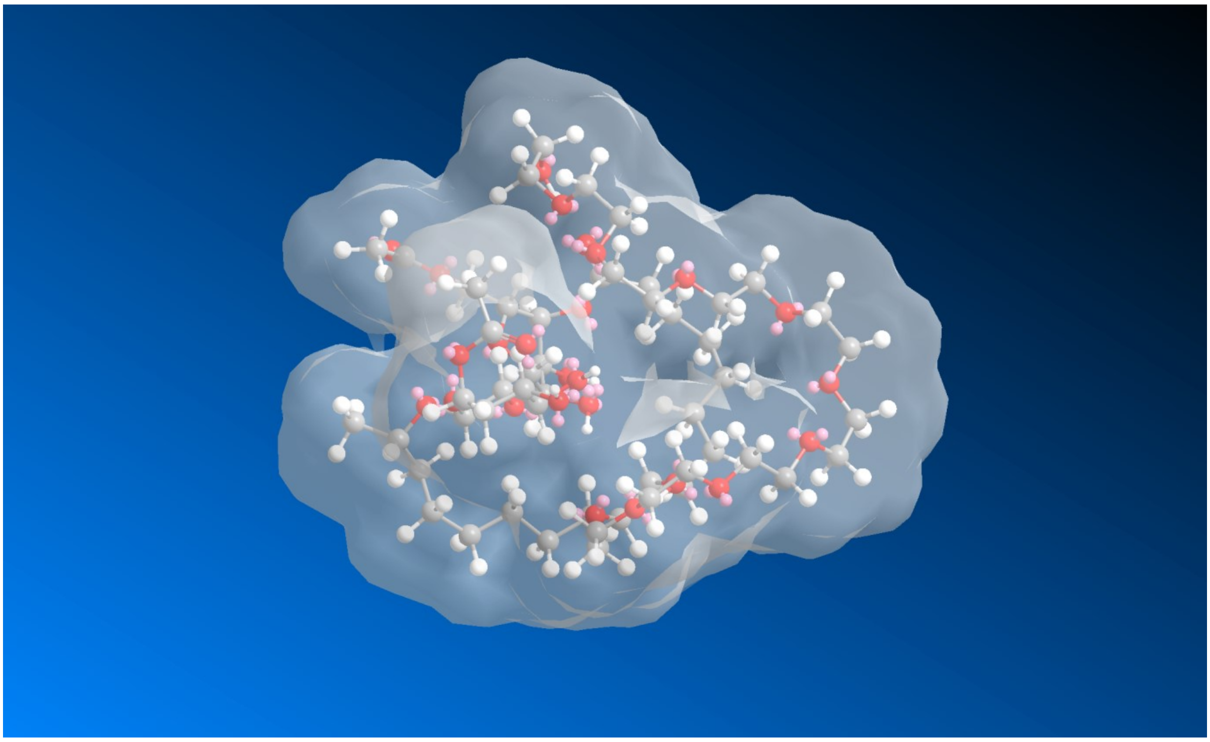
3D – unmodified



3D – unmodified – showing surface



Optimised molecular dynamics



Optimised molecular dynamics – showing surface