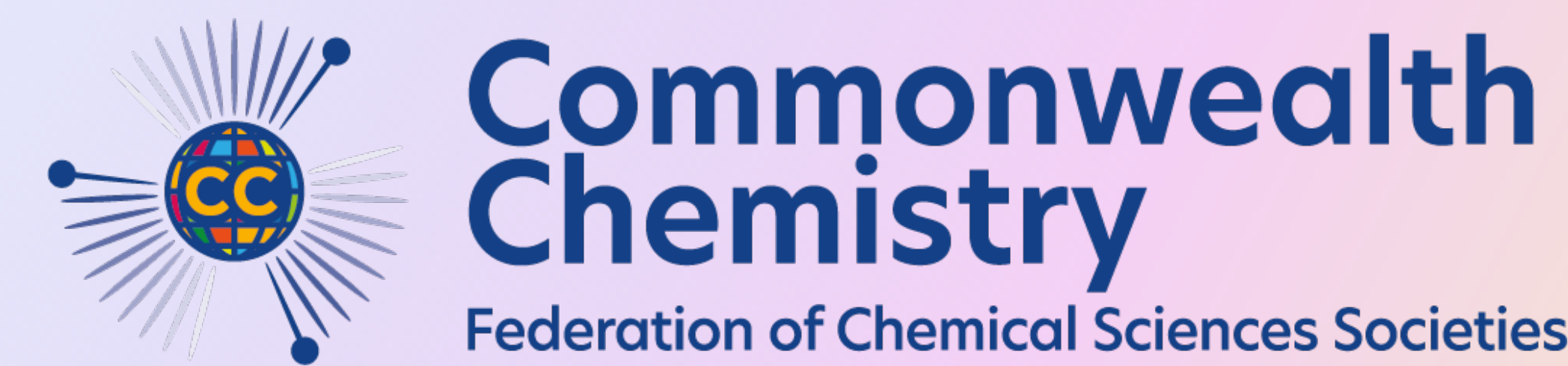
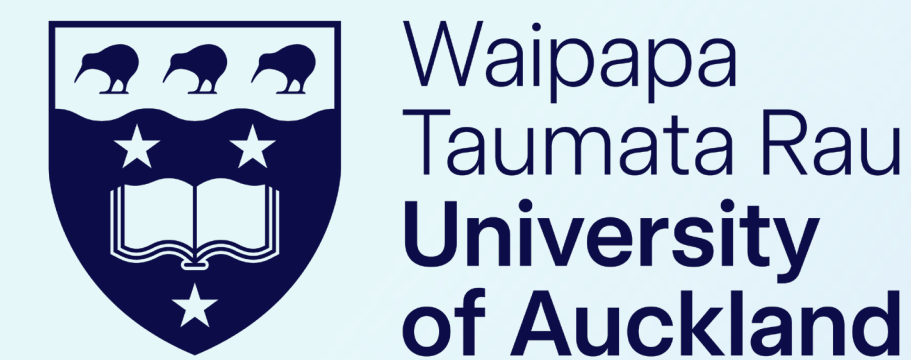


Renewable Platforms for Bio-Based Surfactants

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Introduction

Surfactants

Surfactants are amphiphilic substances with the ability to lower the surface tension at the water-oil interface.¹

- Notable for their surface activity
- Used widely by individuals and industry²

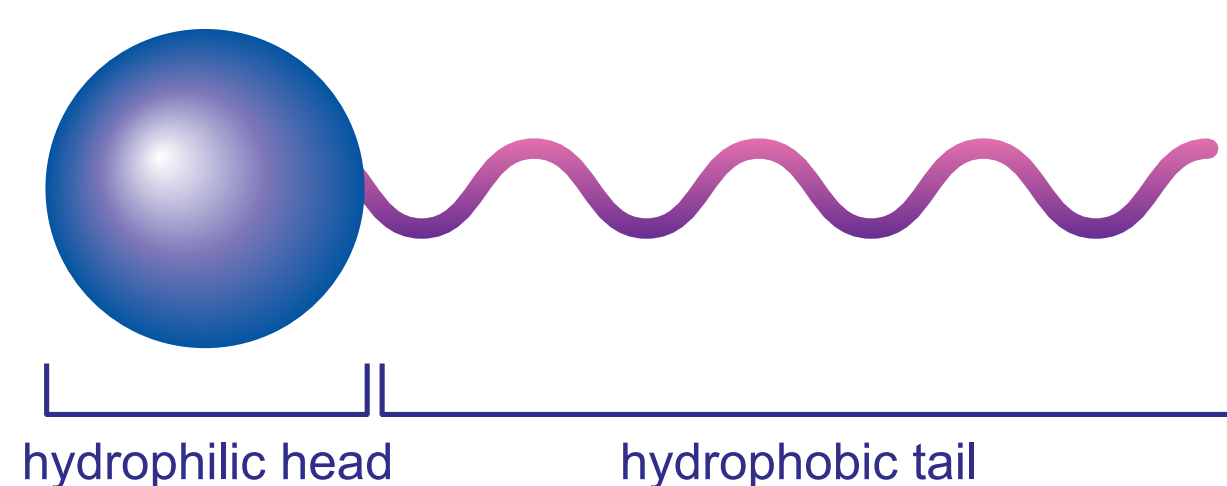


Figure 1. The general structure of a surfactant. The tail is usually bio-based, but the head is often not, offering opportunities for greener design.³

Surface tension characterisation

Critical micelle concentrations (CMCs)

- Most common way to measure surfactant efficacy.
- As surfactant concentration increases, the surface tension of the solution decreases.
- Surfactants start forming micelles at the concentration known as the CMC, and a plateau in the reduction in surface tension is observed.

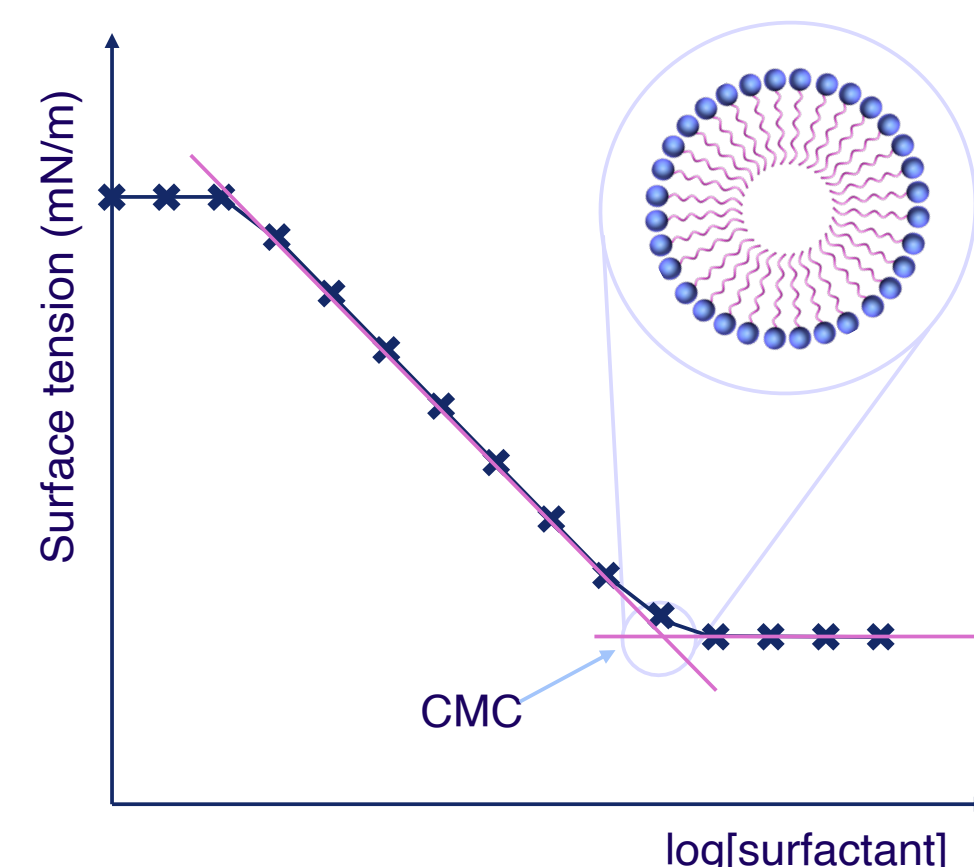


Figure 2. The CMC is found where surface tension reduction and its plateau intersect.

A shift towards bio-based synthons

Chemical synthesis is highly reliant on fossil fuels, which comprise 90% of the chemicals market.⁴ With rising concerns over the adverse effects of fossil fuel use,⁵ bio-based synthons have become increasingly desirable.⁶

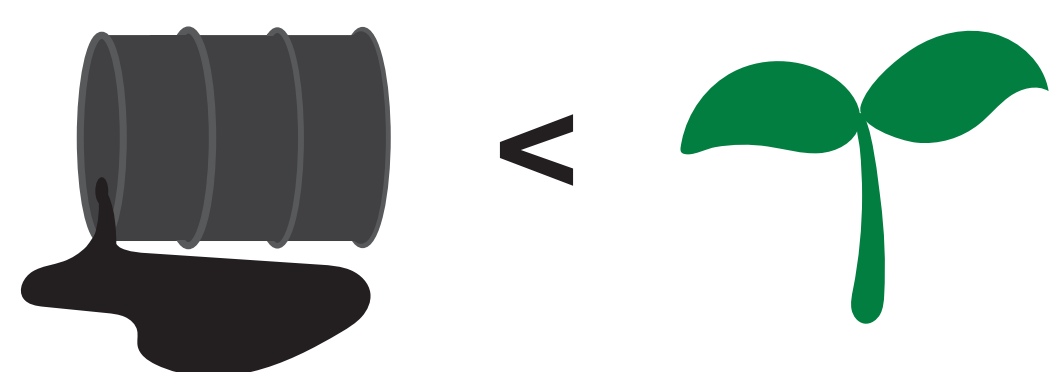


Figure 3. Growing concerns over fossil fuels has favoured the development of bio-based synthons.

Bio-based synthons have various advantages³ over their fossil fuel counterparts:

- Renewable
- Can be derived from waste streams
- Naturally-occurring functional groups
- Generally more easily biodegradable

Levoglucosenone (LGO) as a bio-based synthon

Lignocellulosic biomass is produced as a byproduct from agriculture, horticulture, and forestry.⁷

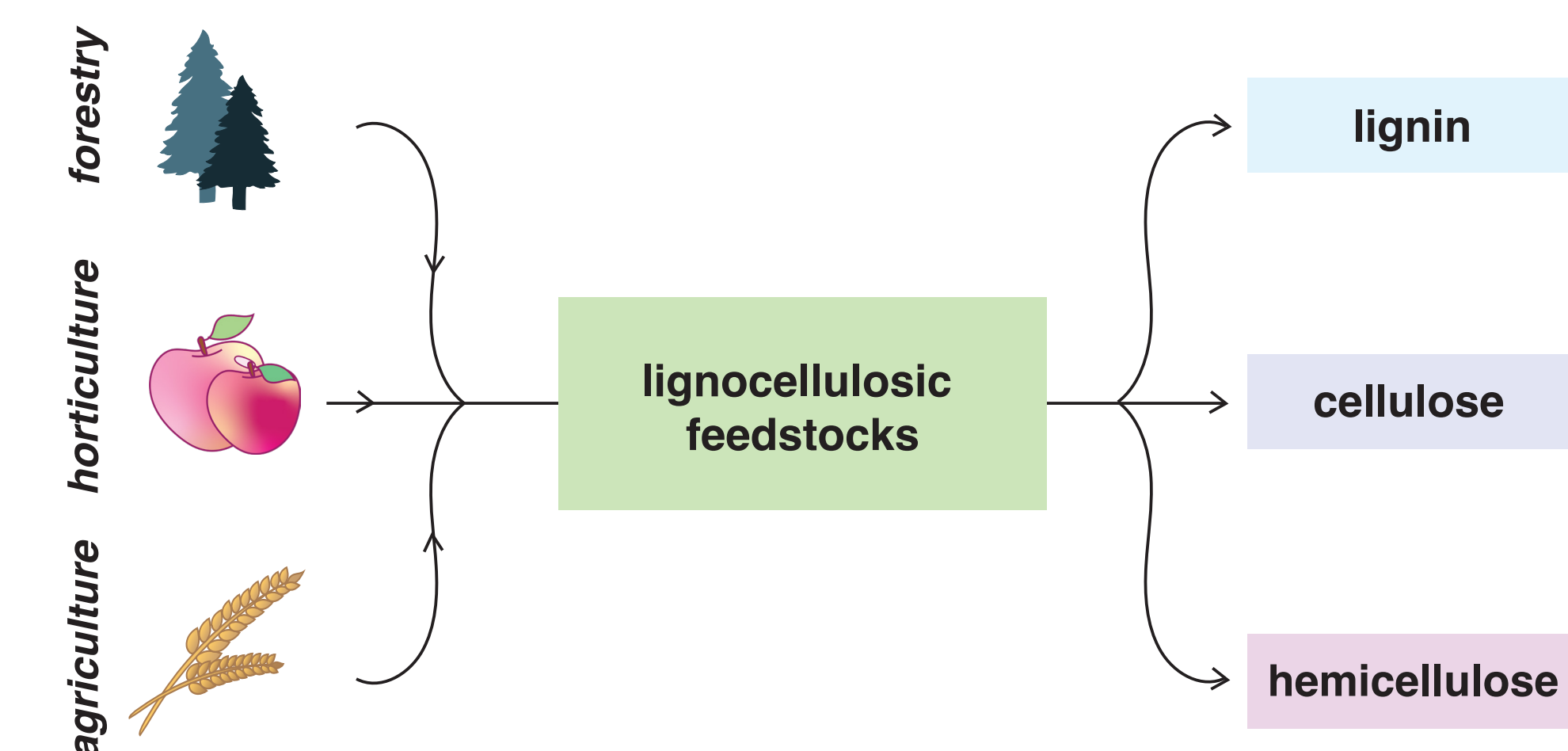
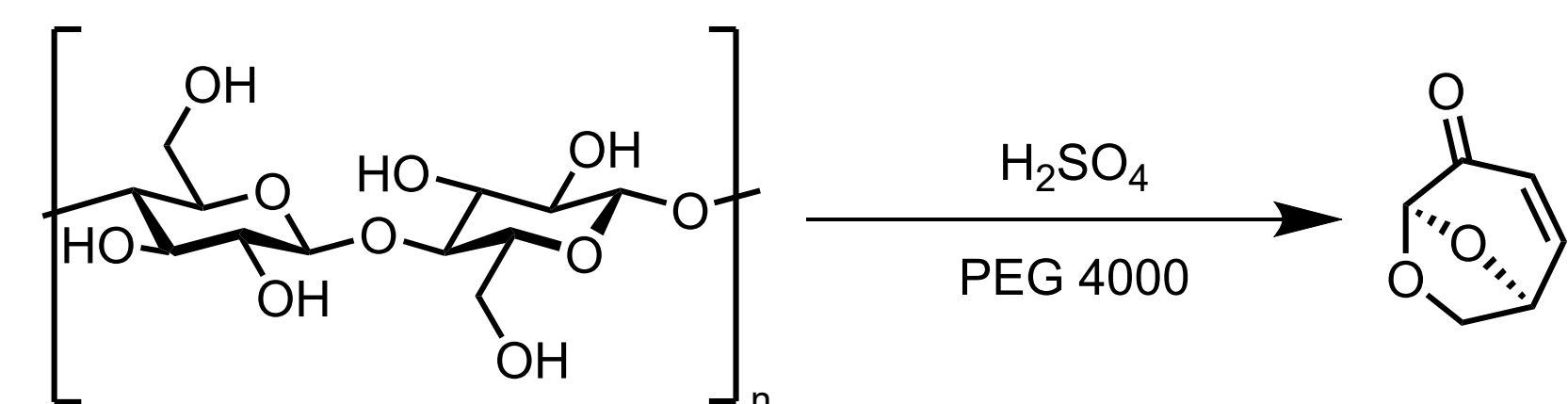


Figure 4. Industry waste can be converted into valuable chemical synthons.

Cellulose is a major component of biomass, from which LGO can be produced as an acid pyrolysis product.⁸



Scheme 1. Acid-catalysed pyrolysis of cellulose to obtain LGO.

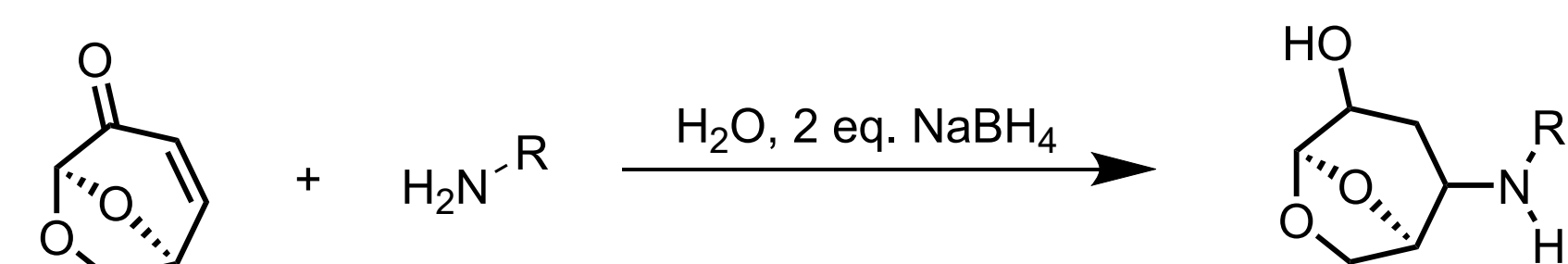
The intention of this work is to create novel bio-based surfactants, replacing the petrochemical-based head groups currently used. These surfactants will then be assessed for their performance and biodegradability.

Methods

LGO-based surfactant synthesis

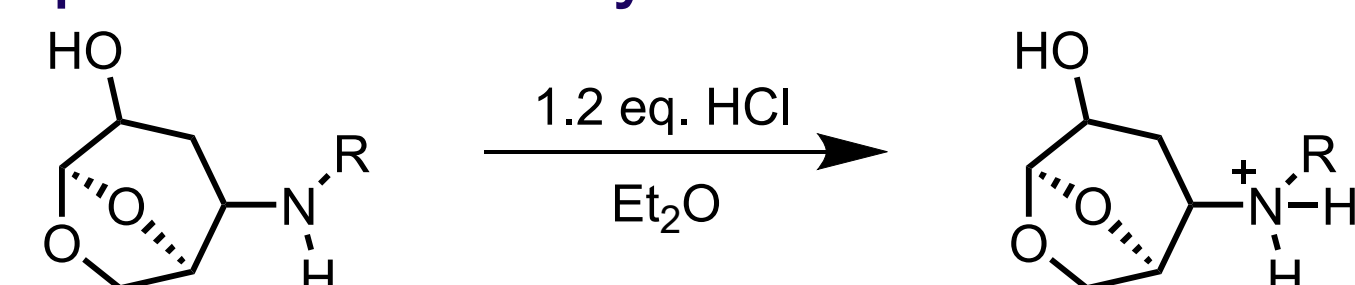
Aza-Michael additions

Aza-Michael additions were used to attach amines of various chain lengths to LGO.



Scheme 2. Aza-Michael addition of linear amines to LGO. R = butyl (LGOBut), hexyl (LGOHex), octyl (LGOOct), decyl (LGODec).

- Products had limited water solubility, preventing the determination of a CMC value (see *Surface tension characterisation*)
- LGOOct and LGODec were then protonated to improve aqueous solubility

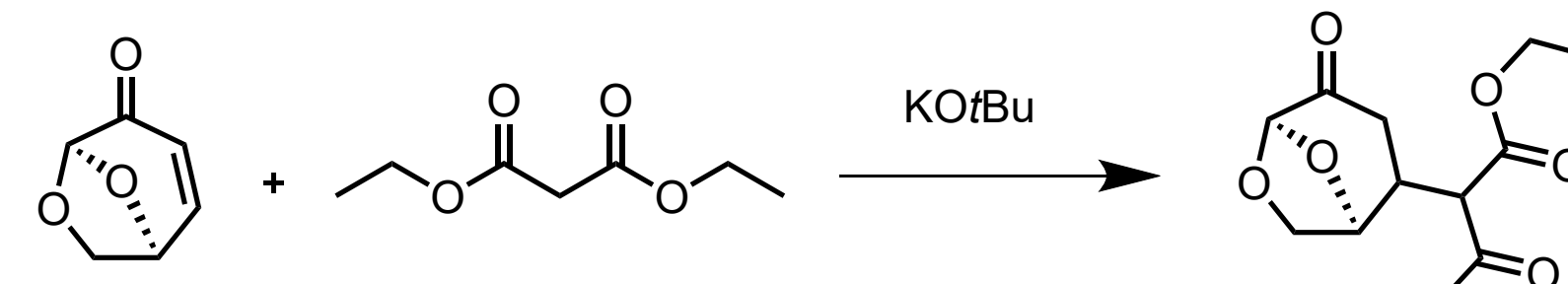


Scheme 3. Protonation of LGO amines into their corresponding HCl salts.

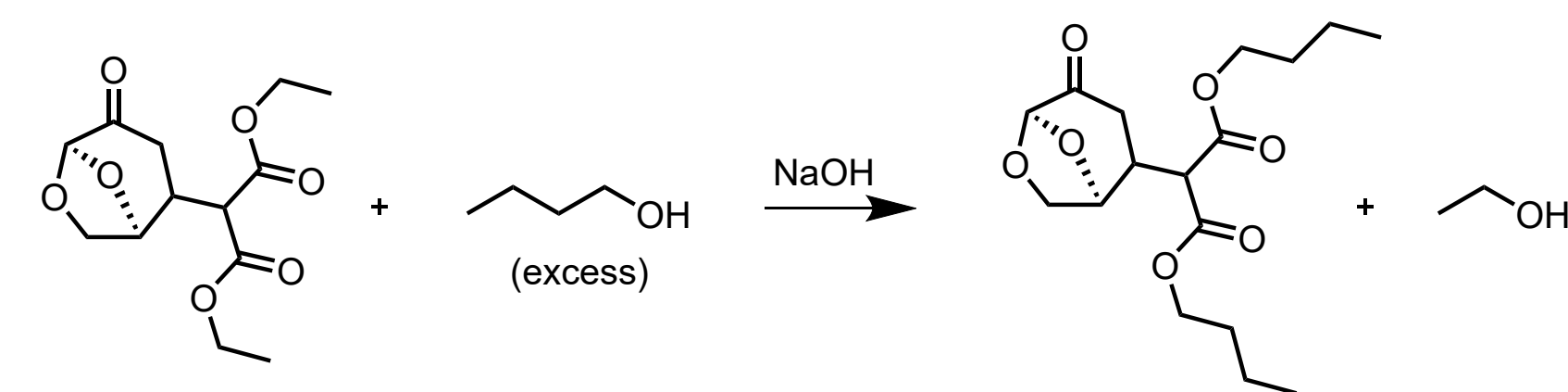
Malonate ester addition

Malonate esters were explored for their potential as two-tailed surfactants.

- Diethyl malonate was added to LGO via Michael addition (Scheme 4)
- Butyl groups were added via transesterification (Scheme 5)



Scheme 4. Michael addition of diethyl malonate to LGO.



Scheme 5. Transesterification of LGODEM into the dibutyl malonate, LGODBM.

Surface tension characterisation

The surface tension of all products at various concentrations was measured.

Surface tension behaviour of LGO amines at various concentrations

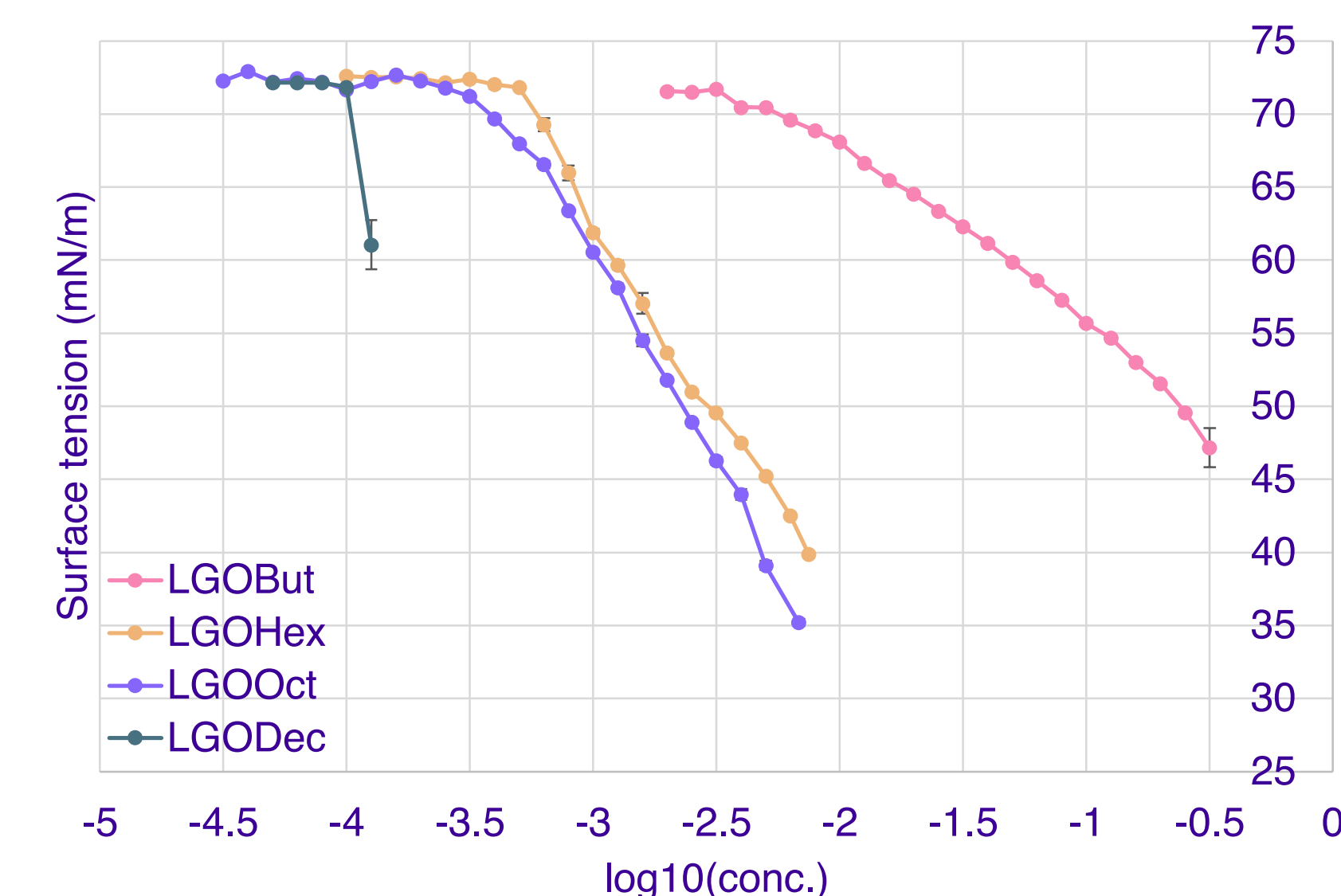


Figure 5. While the LGO amine products show surface active behaviour, a CMC is not observed.

Surface tension behaviour of protonated LGOOct and LGODec at various concentrations

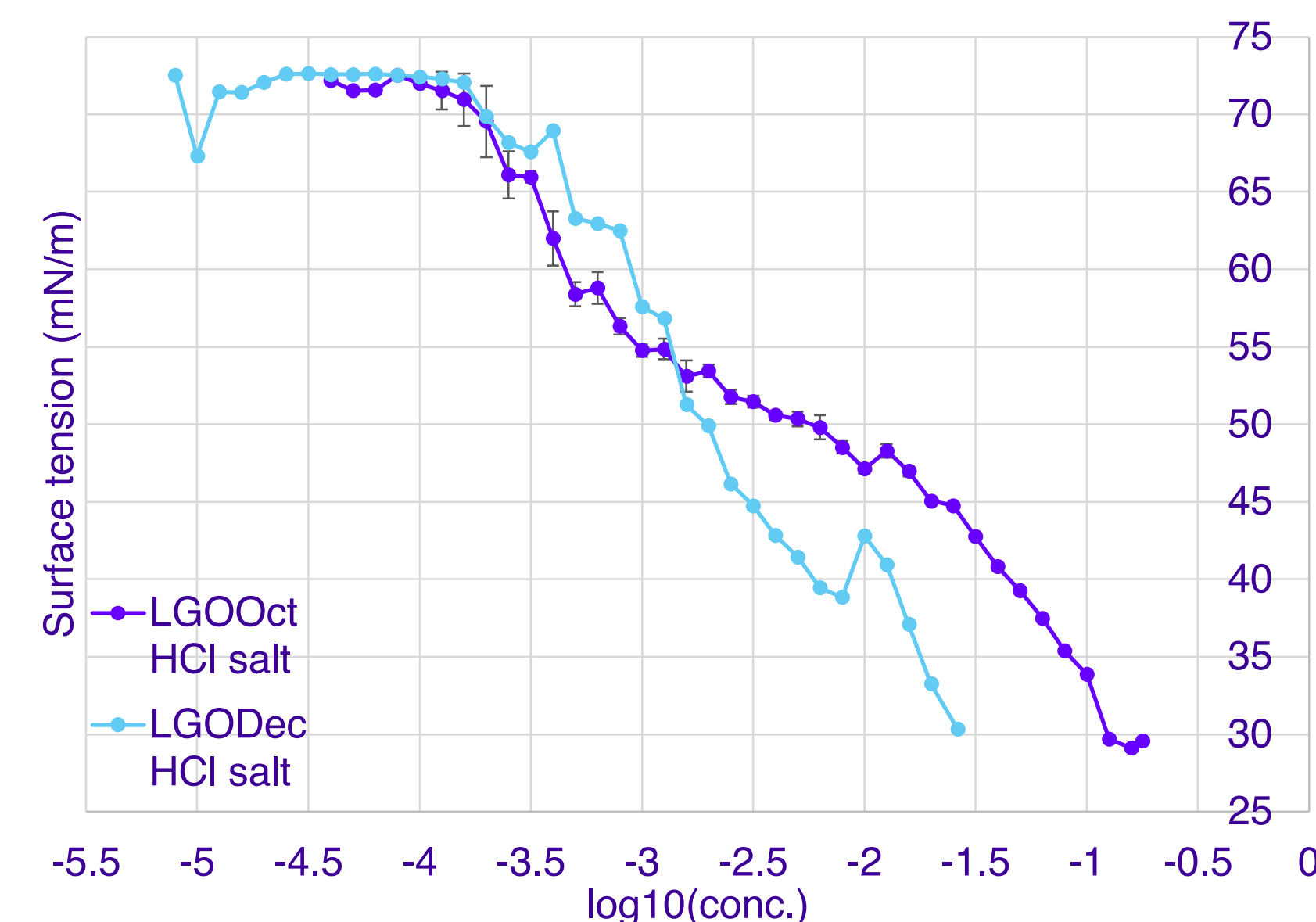


Figure 6. LGOOct and LGODec salts show greater solubility, but a CMC region is still not observed.

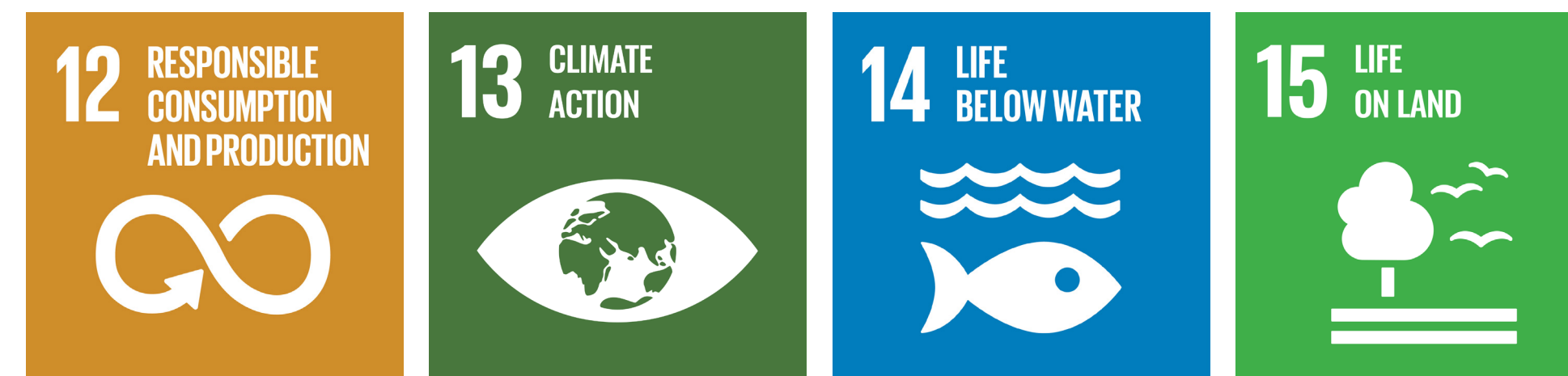
Although all synthesised single-tailed surfactants showed promising surface activity, they do not appear to form micelles even at their highest solubility. The double-tailed malonate surfactants also suffer solubility issues, indicating that a more hydrophilic head-group may be necessary for micelle formation.

Conclusions

Sustainable Development Goals (SDGs)

This work is in alignment with several of the UN SDGs.

- Reducing fossil fuel reliance and increasing waste valorisation ensures more sustainable consumption and production patterns, fulfilling **SDG 12**
- Fossil fuel use is a primary driver of anthropogenic climate change, while landfill is another major contributor of greenhouse gases. Diverting from waste to replace fossil fuel sources aligns with **SDG 13**
- Petrochemical use and distribution has associated harms such as water pollution and ecosystem disruption. Using synthons derived from industrial by-products, designed to degrade in the environment, this work is in alignment with **SDGs 14 & 15**



Future work

The exploration of other bio-based hydrophilic head groups may resolve the solubility issues and allow for micelle formation. For the best performing surfactants, biodegradation studies will be conducted to verify the fates of surfactants after disposal.

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