



Fig. 2 Average droplet size of DES in water (30 : 70 volume ratio) emulsions stabilised with either 1.5 wt% OCNF or C8-OCNF, error bars based on standard deviation of repeat measurements.

OCNF, and reduce the energy necessary to create a new interface, thus improving homogenization. This could allow tighter packing around the droplets, leading to smaller, more stable droplets. Similar effects have been observed for cellulose nanocrystal-stabilised emulsions using standard oils.^{35,36}

While larger droplets may be expected to cream faster due to having a lower density, this was not the case here. The difference in creaming between OCNF and C8-OCNF is due to the higher viscosity of the continuous phase of OCNF- over C8-OCNF-stabilised emulsions which works to prevent creaming (Fig. S2†).²² Increased viscosity comes from the higher surface charge of OCNF compared to C8-OCNF, which increases the excluded volume.

Previous emulsion research demonstrated that cellulose nanofibrils with higher charge provided greater stability than lower charged fibrils.²³ The method of hydrophobisation used here necessitates the replacement of some of the negative carboxylate groups with hydrophobic chains, thus reducing the ζ potential from -60 mV to -43 mV. This would reduce repulsion between fibrils, and allow movement of droplets, ultimately leading to creaming.

In comparison, emulsions stabilised with soluble starch polymers, rather than cellulose particles, which have an even smaller ζ potential (-14 ± 1 mV)³⁷ creamed on day 2. By day 23 there was precipitation and clumping and the mean droplet size was over $20 \mu\text{m}$ (Fig. S3†).

Small angle X-ray scattering (SAXS) was used to investigate the structure of these emulsions. Fig. 3 shows the scattering patterns for OCNF and C8-OCNF in water and for the DES in water emulsions.

The scattering pattern of OCNF in water can be fit with an elliptical cylinder model with a minor radius of $12.4 \pm 2 \text{ \AA}$ and a major radius of $58 \pm 9 \text{ \AA}$, in line with previous research.³² The same model can be used to fit the majority of the data for the emulsion sample, with a minor radius ($13.4 \pm 2 \text{ \AA}$) and a major radius ($66 \pm 9 \text{ \AA}$) that are within the error for OCNF fibrils in

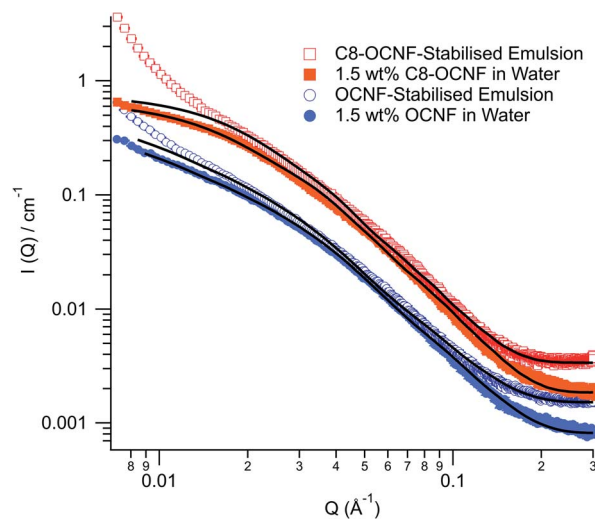


Fig. 3 SAXS patterns of 1.5 wt% OCNF (filled circles) or C8-OCNF (filled squares) in water, and the DES in water emulsions stabilised by either 1.5 wt% OCNF (open circles) or C8-OCNF (open squares). Model fits are shown as black lines (parameters given in ESI†).

water, suggesting that the OCNF fibrils are dominating the SAXS signal.

The scattering pattern for C8-OCNF in water can be fit with the same parameters as OCNF except that the length is significantly shorter (300 ± 20 compared to $>1000 \text{ \AA}$). Given the benign nature of the modification procedure, this apparent change in length is most likely a result of fibril flocs. The length reported by SAXS is actually the distance between intersection points rather than an actual shortening of the fibrils (see Fig. S5†). Similar aggregation has been observed for nanocrystalline cellulose upon addition of salt to screen repulsive charges.³⁸ As with OCNF, the SAXS data from the emulsion stabilised by C8-OCNF can be fit with a similar model.

As shown in Fig. 3, the scattering from both emulsion samples have an upturn at low q which cannot be fitted with the elliptical cylinder model. This is probably from the emulsion droplets. Based on the laser diffraction data, these droplets are far outside of the probed range of this SAXS instrument and so cannot be fitted. The upturn appears to happen at higher q for the C8-OCNF stabilised emulsions, indicative of smaller droplets, which is consistent with the laser diffraction results. Also, due to the smaller surface charge, C8-OCNF is prone to self-aggregation, which could also contribute to the low- q signal.

The SAXS results demonstrate that for both OCNF and C8-OCNF the cellulose nanofibril structure is unchanged in the presence of the hydrophobic DES, compared to in water dispersions.

For the purposes of completeness, DES in water emulsions were also made with more traditional surfactants (dioctyl sodium sulfosuccinate (AOT) or Tween20). This produced emulsions with even smaller droplets ($\sim 0.2\text{--}0.6 \mu\text{m}$) that remained stable for more than 60 days (see ESI†). However, the emulsion stabilised with AOT broke down by day 100, with separate oil and water layers. The emulsion stabilised with



