Effect of 1-hexanol on C$_{12}$E$_{10}$ micelles: a molecular simulations and light scattering study†

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The micelles of non-ionic C$_{12}$E$_{10}$ surfactant and 1-hexanol as an aqueous solution additive are studied toward the purpose of understanding the role of alcohol additives in tuning the characteristics of alkyl-ethoxylate micellar systems. Our dynamic light scattering and cloud point experiments show that the addition of hexanol induces a response similar to increase of temperature. We associate the change with increased attraction between the micelles at low to moderate hexanol loadings and a potential increase of aggregate size at high hexanol-to-surfactant ratio. Detailed molecular dynamic simulations characterization shows hexanol solubilizes to the micelle palisade layer when the hexanol-to-C$_{12}$E$_{10}$ ratio is less than or equal to 0.5, while swollen micelles, in which a part of the hexanol forms an oil core, are present when the ratio increases above approximately 1.5. The simulations indicate that the surface of the micelles is rough. Formation of reverse hexanol structures akin to those found in bulk octanol is observed in the oil core. The molecular simulations associate the experimentally deduced increase in attraction between the aggregates to result from dilution of the headgroup region due to hexanol acting as a spacer molecule between neighbouring surfactants. Altogether, the findings provide a detailed physical characterization of the effect of an archetypal solution additive, hexanol, on an alkyl ethoxylate micelle system. The findings could bear significance in designing micellar and emulsion based systems with desired solution characteristics or properties for e.g. drug delivery, catalysis, or platforms for green chemistry reactions.

Introduction

Surfactants and their micelles are immensely important in bio and food technology, cleaning (detergents), textiles, cosmetics, paper and paint production, as well as, in mining (flotation). They also bear fundamental significance in basic biological processes. This variety of uses and importance of surfactants roots from the diversity and dynamics of their assembly morphologies. In aqueous solutions, these include structures such as spherical micelles, rod-like micelles, vesicles, bilayers, and various hexagonal phases.$^{1-4}$ Specifically micellar aggregation morphologies, as well as, their dynamics and transitions, are important for the use of surfactants as carriers for active compounds, e.g., therapeutic or biologically active molecules, for achieving desired characteristics of paints, personal care and food products, as well as, for generating confined and controlled reactions platforms in aqueous green chemistry environments, see e.g.$^{5-11}$

Here, we examine micellar aggregation and the aggregate structural response of polyethylene glycol (PEG) based non-ionic surfactants with the general formula C$_i$E$_j$, alkyl ethoxylates, in aqueous solution. The $i$ and $j$ correspond to the number of methylene C and ethoxylate groups E in the hydrophobic tail and hydrophilic headgroup, respectively. Alkyl ethoxylate surfactants and their aggregation response are commonly used in detergents, personal care products, and in industrial processes especially in agriculture, textile, paper, and oil industries.$^{12}$ Alkyl ethoxylates are particularly interesting because of their relatively simple chemical structure and biocompatibility.

Upon heating, micelles of alkyl ethoxylates exhibit elongation, aggregate growth, and increased intermicellar attractivity, which culminates to liquid-liquid phase separation at a temperature commonly known as the cloud point. The response can be controlled to some extent by modifying the surfactant structure: larger headgroup typically means a higher cloud point temperature and smaller micelle size, while an increase in the tail length has an opposite effect, see e.g. Refs.$^{13,14}$ for reviews. For instance, C$_{12}$E$_5$ has a cloud point of 32°C and exhibits strong mi-
cellar growth and morphological changes as temperature is increased towards the cloud point. 

To improve the performance and properties of the alkyl ethoxylate surfactant solutions, various additives such as alcohols, inorganic salts, and sugars are commonly used as solution additives to the pure surfactant solution. Perhaps the most frequently used additives are aliphatic alcohols as they can act as cosurfactants. Generally, short-chain alcohols remain in the bulk aqueous solution, but can indirectly influence the morphology of surfactant aggregates by modifying the hydrophobicity of the solvent. On the other hand, long-chain alcohols partition within the micelle and induce morphological changes due to the modified surfactant packing. The effect of alcohols on the microstructure of ionic surfactants has been the subject of extensive research, but for non-ionic surfactants, with the notable exception of Pluronics, the focus has been on the effect of alcohols on cloud point. Additionally, isolated studies concerning the effect of alcohols on the morphology and interactions of micelles composed of alkyl ethoxylates, sugar surfactants, and Triton X-100 exist.

Despite the vast amount of experimental work characterizing both pure C\(_{12}\)E\(_{10}\) solutions and the effect of additives, the molecular-level mechanisms underlying the observed solution responses are still not well understood. For instance, changes in micellar morphology and intermicellar interactions yield similar responses in many experimental techniques such as dynamic light scattering (DLS) and viscometry. This leads to, e.g. the proportion of effects rising from micellar growth and intermicellar attraction in observed solution response, as well as their respective mechanisms, to remain poorly identified.

Theoretical calculations and computer simulations could be at key position in differentiating between the molecular interactions and advancing understanding on these systems, but curiously relatively few studies exist on micellar systems of alkyl ethoxylates. Sterpone et al. have used atomistic detail molecular models to study the structural response of preassembled C\(_{12}\)E\(_{10}\) micelles to temperature and pressure, while Iyer et al. have studied the energetics of C\(_{12}\)E\(_{4}\)/C\(_{12}\)E\(_{10}\) mixed micelles. These studies cover basic structural and energetics response. However, to our knowledge, charting effect of any additives on alkyl ethoxylate micelles via computational means is lacking: this is surprising as molecular simulations could identify the origins of the changes in solution characteristics that the use of solution additives aims at.

Here, we contribute to filling this gap by characterizing the effect of 1-hexanol to the structure of C\(_{12}\)E\(_{10}\) micelles by light scattering experiments and molecular dynamics simulations in all-atom detail. We analyze in detail the structural response to variations in C\(_{12}\)E\(_{10}\) and hexanol concentrations in this model system and associate the observations with changes in intermicellar attraction. The surfactant C\(_{12}\)E\(_{10}\) is chosen as the alkyl ethoxylate species for the study because of its relatively small size that enables studying computationally the response of systems composed of several aggregates in atomistic detail and because C\(_{12}\)E\(_{10}\) micelles have been studied experimentally significantly. The surfactant C\(_{12}\)E\(_{10}\) is composed of a twelve carbon long hydrophobic moiety and a relatively bulky ten ethoxylate groups long polyethylene glycol chain, yielding a low critical micelle concentration, high cloud point and a relatively compact micelle size. While related surfactants with smaller headgroups exhibit considerable elongation and micellar growth when cloud point is approached (see e.g. Refs. 17–19, 48), evidence suggests that the headgroup of C\(_{12}\)E\(_{10}\) is sufficiently big to largely prevent such growth from taking place. However, reports on modest micelle elongation upon addition of potassium iodide and sugars exist. Hexanol is chosen for the model aliphatic alcohol additive of the study because it presents a typical, commonly used medium chain alcohol additive, because of its fast dynamics in water solutions, and because of its known capacity to act as a cosurfactant in micellar systems.

**Methods**

**Simulations.** The simulations employed GROMOS 53A6\(xy\)-D united-atom force field, SPC/E explicit water model and GROMACS 5.0 simulation software. Long-range electrostatics were treated by the PME algorithm, while for the Lennard-Jones interactions the twin-range cutoff scheme of GROMOS was used (0.8 nm and 1.4 nm). Constant temperature and pressure conditions were obtained by using the stochastic velocity rescaling thermostat of Bussi et al. (\(\tau_T = 0.5\) ps, \(T_{ref} = 298\) K) and the Parrinello-Rahman barostat (\(\tau_P = 2\) ps, \(P_{ref} = 1\) bar). VMD was used for the visualization.

The micelles formed in 200–400 ns self-assembly simulations from random solutions of 200 C\(_{12}\)E\(_{10}\) molecules (~12 wt % or ~200 mM C\(_{12}\)E\(_{10}\) concentration) in pure water or with hexanol (HxOH) added at hexanol-to-surfactant molar ratios HxOH:C\(_{12}\)E\(_{10}\) of 0.25, 0.50, 1.50, and 2.50. To probe the sensitivity to initial configuration, simulations corresponding to the same molecular composition but starting from multiple different initial configurations were conducted for the pure C\(_{12}\)E\(_{10}\) system and for the system with hexanol-to-surfactant ratio 0.5. Finally, the sensitivity of micellar morphology to surfactant concentration was evaluated by a simulation at 15 wt % C\(_{12}\)E\(_{10}\) concentration.

To obtain data unperturbed by micelle-micelle interactions, a set of micelles including their solvation shells (1 nm) were extracted from the simulations, resolvented with water, and simulated for an additional 40 ns. The set was chosen so that the selected micelles cover all micelle sizes present in the simulations. Additionally, large pure C\(_{12}\)E\(_{10}\) micelles were constructed from the micelles formed in the presence of hexanol by extracting the micelle from the self-assembly simulations and then removing all hexanol molecules. The first 5 ns (20 ns for the large, pure C\(_{12}\)E\(_{10}\) micelles formed by removing hexanol) was considered the initial relaxation period, and was disregarded in the data analysis.

The micelles were characterized from the simulations in terms of radius of gyration \(R_g\), hydrodynamic radius \(R_{Ht}\), hydrocarbon core radius \(R_{Hc}\) and hydrocarbon core length \(L\). Two shape parameters, the aggregate eccentricity \(e\) and the rod-to-disk parameter \(s\) were calculated for the micelles. Here, the eccentricity \(e\) is
defined
\[ e = 1 - \frac{I_l}{I} \]  
where \( I_l \) is the smallest principal moment of inertia and \( (I) \) the mean inertia moment. The rod-to-disk parameter \( s \) is given by
\[ s = \frac{I_3 - I_2}{I_3 - I_1} \]  
where \( I_i \) is the \( i \)th principal moment of inertia. For rod-like particles, \( s = 0 \) while for disk-like, \( s = 1 \). Core radius \( R_{hc} \) was determined as the peak position of the radial distribution function calculated for the micelle center of mass and the methylene group next to the surfactant head. The rod-like micelles were oriented along the \( z \)-axis and the radius calculated in the \( xy \)-plane only. Length of the micelle \( L \) was estimated by calculating the density profile and its derivative along the principal axis of the micelle and using the distance between the peaks in the derivative as \( L \). Area per surfactant \( A \) is calculated for the micelle center of mass and the methylene group and using the distance between the peaks in the derivative as \( L \). Hydrodynamic radius \( R_H \) of the simulated micelles was estimated from the radius of gyration \( R_g \) according to
\[ R_H = \sqrt{\frac{5}{3} R_g} \]  
We note that this is a crude approximation of the true, diffusion-based \( R_H \). However, calculation of the micellar diffusion coefficients necessary for determining \( R_H \) based on diffusion is not realistic at the simulated time scales.

Ordering of the acyl chains was characterized by using the C-H bond order parameter \( S_{CH} \) as the measure of ordering. For micelles, the C-H bond order parameter can be extracted experimentally from multi-field NMR measurements. From simulations, it is calculated via defining an order parameter tensor \( S_{ij} \)
\[ S_{ij} = \frac{1}{2} \alpha \cos \theta_{ij} - \delta_{ij} \]  
where \( \theta_{ij} \) is the angle between \( i \)th axis in the local molecular frame and the vector perpendicular to the local micelle surface (local normal vector). The local molecular frame for each tail carbon atom is defined (in Cartesian coordinate system) by the \( z \) coordinate axis being along the \( C_{n-1} \) to \( C_{n+1} \) vector, \( x \) being normal to the plane defined by \( C_{n-1}, C_n \) and \( C_{n+1}, \) and \( y \) being along the bisector of the angle \( C_{n-1}, C_n, C_{n+1} \). This constitutes the way for defining the local coordinate frame for united-atom chains. The local micelle surface normal vector for each surfactant is defined here as the vector from the center of mass of the micelle to the first ethoxylate group oxygen of the chain. Order parameter \( S_{CH} \) compatible with the experimentally measurable C-H order parameter can then be computed using the formula
\[ S_{CH} = \frac{2}{3} S_{xx} + \frac{1}{3} S_{yy} \]  
\( S_{CH} \) = −0.5 corresponds to full order perpendicular to the director, \( S_{CH} = 1.0 \) to full order along the director, and \( S_{CH} = 0 \) to an isotropic distribution.

Hydrogen bonds were counted using the default geometric criterion in GROMACS: the donor-acceptor cutoff \( r_{DA} \) = 0.35 nm and angle \( \theta_{HDA} = 30^\circ \). The lifetime of the bonds were approximated as the integral of the bond autocorrelation function. Lifetimes were normalized with the average water-water hydrogen bond lifetime.

**Experimental.** Decaethylene glycol monododecyl ether \( (C_{12}E_{10}) \) was purchased from Sigma-Aldrich and laboratory grade 1-hexanol (n-hexanol) from JT Baker Chemical Co. The surfactant solutions were prepared by weight. The water used in all experiments was 18.2 MO-cm (Milli-Q) water. Samples were allowed to equilibrate overnight at room temperature.

Dynamic light scattering (DLS) experiments were performed using a Malvern Zetasizer Nano ZS at a 173° back-scattering configuration. The temperature was 25°C, unless otherwise stated. The intensity-averaged diffusion coefficient \( D \) was inferred from the correlation function via cumulants analysis and the apparent hydrodynamic radius \( R_H \) was then evaluated using the Stokes-Einstein equation.

The cloud point temperatures \( T_{CP} \) were determined by heating 2 mL samples in an oven (0.2°C temperature stability) at the rate of 1°C/10 min. The temperature at which the samples turned visually turbid was taken as the cloud point temperature.

**Results**

**Experimental.** To obtain initial insight on the \( C_{12}E_{10} \) solution response to changes in \( C_{12}E_{10} \) concentration and the addition of 1-hexanol, we carried out basic DLS and cloud point measurements experimentally. Addition of hexanol can be expected to lower the cloud point, increase intermicellar attractivity, and either promote micelle elongation or form swollen micelles with \( C_{12}E_{10} \). Figure 1 shows the measured apparent hydrodynamic radius \( R_H \) and \( T_{CP} \) of micellar \( C_{12}E_{10} \) solutions at different hexanol-to-surfactant molar ratios \( (\alpha=[HxOH]/[C_{12}E_{10}]) \) for different wt % \( C_{12}E_{10} \) solutions. In all examined samples, the \( C_{12}E_{10} \) concentration exceeds the CMC of \( C_{12}E_{10} \) (12.7 μM). Hence, micellization and aggregate formation can be expected.

The \( R_H \) data in Figure 1 indicates that the effective hydrodynamic radius of the formed aggregates is initially insensitive to the addition of hexanol but at a \( C_{12}E_{10} \) concentration-dependent hexanol-to-surfactant ratio \( \alpha^* \), \( R_H \) starts to increase with any further added hexanol. This change in the aggregate characteristics and the system response to added hexanol at the critical hexanol-

Table 1 Simulated self-assembly systems. The table summarizes for each simulation the system name, the hexanol-to-surfactant molar ratios \( [\text{HxOH}]/[C_{12}E_{10}] \), the numbers of \( C_{12}E_{10} \) molecules \( N_{C_{12}E_{10}} \), hexanol molecules \( N_{\text{Hex}} \), and water molecules \( N_{\text{H}_{2}O} \), as well as, the total simulation time. Concentration of \( C_{12}E_{10} \) is ∼12 wt % except ∼15 wt % in the simulation A+.

<table>
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<th>System name</th>
<th>[HxOH]</th>
<th>( N_{C_{12}E_{10}} )</th>
<th>( N_{\text{Hex}} )</th>
<th>( N_{\text{H}_{2}O} )</th>
<th>Time (ns)</th>
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<tr>
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<td>500</td>
<td>45788</td>
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to-surfactant ratio $\alpha = \alpha^*$ can result from either aggregate size or shape change, or increased attraction between them, or a combination of these: changes in aggregate morphology and intermicellar interactions yield similar measurement response.

Figure 1b shows the corresponding cloud point temperature $T_{CP}$ results. As expected, increasing C$_{12}$E$_{10}$ concentration works toward decreasing $T_{CP}$. Likewise, the addition of hexanol decreases $T_{CP}$. The data reveals that the DLS measurement temperature, 25°C, is consistently below the cloud point temperature $T_{CP}$. Besides increasing the temperature above the cloud point, phase separation could be achieved also via the amount of added hexanol exceeding the maximum solubility of hexanol. However, the resulting phase separation was distinct from cloud point response as slight warming resulted in solubilization. At 12 wt % C$_{12}$E$_{10}$ concentration, the maximum solubility of hexanol was determined to be $\alpha = 2.5 - 2.7$ at room temperature. At low C$_{12}$E$_{10}$ concentrations (1 wt % and 2 wt %), maximum hexanol solubility was marked by the emergence of tiny hexanol droplets; the exact solubility was not determined. Altogether, the $T_{CP}$ mapping as the function of concentration and hexanol content, Figure 1b, reveals that the observed change in $R_1$ response at $\alpha^*$ is not related with the cloud point transition. However, the data also shows that the aggregate interactions in the system upon addition of hexanol do bear significant temperature dependence.

It is instructive to note that the threshold hexanol-to-surfactant ratio $\alpha^*$ at which the $R_1$ becomes sensitive to added hexanol is not the actual hexanol-to-surfactant ratio in the micelles but in the entire system. This is because of the slight water solubility of hexanol. The actual hexanol-to-surfactant ratio in the micelles $\alpha_{mic}^*$ can be estimated by solving the fraction of micellized hexanol $f_{mic}$ from

$$K = \frac{\gamma_{mic}}{\gamma_{aq}}$$

$$\gamma_{mic} = \frac{f_{mic} \cdot n_{HxOH}}{n_{HxOH} + n_{C_{12}E_{10}}}$$

$$\gamma_{aq} = \left(\frac{1 - f_{mic}}{1 - f_{mic}}\right) \cdot \frac{n_{HxOH}}{n_{HxOH} + n_{HxO}}$$

where $\gamma_{mic}$ and $\gamma_{aq}$ are the mole fractions of hexanol in the micellar and aqueous phase, $K$ the partition coefficient of hexanol calculated between the C$_{12}$E$_{10}$ micelles and the bulk aqueous phase, $\alpha$ is the hexanol-to-surfactant ratio, and $n_i$ the total amount of species $i$ in the system. We note that the above equations assume that water and C$_{12}$E$_{10}$ are constrained to the aqueous and micellar phase, respectively.

Table 2 presents the calculated hexanol-to-surfactant ratio in the micelles $\alpha_{mic}^*$ and the corresponding fractions of micellized hexanol $f_{mic}$. In calculating these, a value for the partition coefficient $K$ is needed. To describe the hexanol partitioning to alkyl ethoxylate micelle corona, the value corresponding to Triton-100 micelles, $\log K = 3.26^{59}$, has been used as an approximation. We are not aware of hexanol partition coefficients for precisely the current system. The data reveals that the concentration dependence of the onset of the $R_1$ increase in Figure 1a results partially from an increase of hexanol in the water solution: about half of

<table>
<thead>
<tr>
<th>$C_{12}$E$_{10}$ (wt%)</th>
<th>$C_{12}$E$_{10}$ (nM)</th>
<th>$R_1$ (nm)</th>
<th>$\alpha^*$ (mol/mol)</th>
<th>$\alpha_{mic}^*$ (mol/mol)</th>
<th>f$_{mic}$ (%)</th>
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<td>0.32</td>
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</table>

Table 2 DLS measured apparent hydrodynamic radius ($R_1$), the threshold [HxOH]$_0$/$[C_{12}E_{10}]_0$ molar ratio $\alpha$ for $R_1$ increase onset, the calculated solubility-corrected [HxOH]$_0$/$[C_{12}E_{10}]_0$ threshold ratio $\alpha_{mic}$, and fraction of micellized 1-hexanol $f_{mic}$ at the different C$_{12}$E$_{10}$ wt % and the corresponding molar concentrations.
although literature data on the be-

swelling at high hexanol-to-surfactant ra-

turnary Information Figure S1). To gain insight on the origins of these changes and to obtain more information of the C$_{12}$E$_{10}$ system response upon addition of hexanol, we next turn to simulations.

Simulations. Molecular dynamics simulations of initially random solutions of pure C$_{12}$E$_{10}$ at 12 wt % and 15 wt % concentrations lead to the formation of approximately spherical micelles with aggregation numbers $N_{agg}$ ranging from 34 to 112. Addition of hexanol, resulted in a wider distribution of aggregate sizes and shapes: at low hexanol-to-surfactant ratios (0.25 and 0.5), spherical and short rod-like aggregates with $N_{agg} = 59 – 200$ are present, while at higher hexanol-to-surfactant ratios (1.5 and 2.5) spherical, swollen micelles with $N_{agg} = 98 – 200$ emerge as the dominant species. Hexanol solubilization into the micelle core takes place at hexanol-to-surfactant ratios between $\alpha = 0.5 – 1.5$ and leads to the formation of an oil core at the highest examined hexanol-to-surfactant ratios 1.5 and 2.5, see Figure 3. At hexanol-to-surfactant ratios below 0.5, hexanol solubilizes exclusively into the palisade layer of the micelles.

For pure C$_{12}$E$_{10}$ micelles, the micelle size range of 34 to 112 C$_{12}$E$_{10}$ molecules in micelle corresponds to a hydrodynamic radius between 2.48 nm and 3.50 nm and a hydrocarbon core radius between 1.33 nm and 1.94 nm, correspondingly. The findings are in good agreement with prior experimental characterizations of pure C$_{12}$E$_{10}$ micelles: mean aggregation numbers ranging between 59 and 125, $^{41-43}$, hydrodynamic radiiues between 2.9 nm and 4.0 nm $^{21,41,44}$ and a core radius of 1.7 nm $^{41}$ have been reported. The increase observed in the hydrocarbon core radius $R_{hc}$ in the simulations with increasing micelle aggregation number is mainly due to the aggregates deviating from spherical shape as the number of surfactants in them increases; this affects the experimental core radius as well.

Figure 4 presents the structural characteristics of the aggregates without and with added hexanol. The dependency of the eccentricity $\epsilon$ and shape parameter $s$ on the aggregation number in Figure 4 shows that in the absence of hexanol and at low hexanol-to-surfactant ratios ($\alpha = 0.25 – 0.5$), the shape of C$_{12}$E$_{10}$ micelles...
Fig. 3 Final configurations of simulations with varying hexanol-to-surfactant molar ratio $\alpha$. Surfactant tails are presented in green, head groups in yellow, and hexanol in gray. Solvent molecules have been omitted for visual clarity. See Figure S2 in the Electronic Supplementary Information for snapshots of the simulations originating from different initial configurations.

Fig. 4 Eccentricity ($e$), rod-to-disk shape parameter ($s$), radius of hydrocarbon core ($R_{hc}$) and area per surfactant ($a$) as a function of aggregation number. Dashed lines are provided as cue to the eye. Black, blue and green indicate no hexanol, low hexanol-to-surfactant ratio ($\alpha = 0.25 - 0.5$) and high hexanol-to-surfactant ratio ($\alpha = 1.5 - 2.5$), respectively. Black squares ($\alpha = 0.00^\circ$) correspond to large, pure C$_{12}$E$_{10}$ micelles obtained from the hexanol self-assembly simulations by removal of hexanol molecules.

Changes from spherical to prolate when the aggregation number exceeds $\sim 100$. These hexanol-to-surfactant ratios correspond to hexanol solubilizing at the palisade layer. On the other hand, the data shows that the solubilization of hexanol into the micelle core, i.e., formation of an oil core at higher $\alpha$ appears to promote spherical aggregate shape and is also associated with a substantial increase in the area per surfactant $\alpha$. Furthermore, the aggregates are dynamic in nature and undergo shape fluctuations over the course of tens of nanoseconds. The reported quantities are mean characteristics which means also the micelles that appear spherical in the data of Figure 4 can bear aspherical shape at any given time.

While the properties of the pure C$_{12}$E$_{10}$ micelles fall within the range of priorly published values, the existence of rod-like micelles in the simulations is seemingly in disagreement with the outcome of our initial experiments and literature based charting of the hexanol response which lead to the deduction of C$_{12}$E$_{10}$ micelles not growing, except potentially at high hexanol content. To understand the simulation results it is first instructive to point out that simulations of this type suffer from statistical uncertainty due to finite-time and finite-size effects (the observed micelles may not represent the equilibrium size and shape distribution). The observed elongated micelles could be random encounters. The shape change can also result from a force field imbalance. We note, however, that prolate micelles with such a low axial ratio as the ones present in the simulations have ($2 < 3$) cannot be discriminated from spherical micelles in the existing electron micrographs and SANS experiments of dilute C$_{12}$E$_{10}$ solutions hint at the possibility of alkyl ethoxylate micelles undergoing modest elongation with temperature even in the case of alkyl ethoxylates with bulky headgroups. Thus, it is plausible that short prolate micelles could exist as part of the natural polydispersity of the micellar distribution at low hexanol-to-surfactant ratio. We stress, however, that the simulations do not support the existence of a sphere-to-rod transition. In the following analysis we concentrate on spherical micelles as these appear to be the dominant form.

To further characterize the effect of hexanol on the micelles, Figure 5 presents radial mass density $\rho(r)$ and average C-H bonds order parameter $S_{CD}$ profiles of three representative spherical micelles formed at different hexanol-to-surfactant ratios. For each hexanol-to-surfactant ratio, a micelle of typical size is chosen; the other spherical micelles show analogous distributions. The mass densities show the average location of a particular molecular species in the micelles and the order parameter captures orientational order of the alkyl chains. For all systems, the density profiles of water, hydrocarbon core, and ethoxylate chains show significant overlap. Although partly this results from spherical averaging and shape fluctuations, the overlap region reflects surface roughness. This is in agreement with recent studies of alkyl and alkylphenyl ethoxylate micelles. Comparison of the micelles formed in hexanol-free, low hexanol-to-surfactant ratio and high hexanol-to-surfactant ratio systems reveals that at low
hexanol-to-surfactant ratios, hexanol is solubilized at the hydrocarbon/water interface but at higher hexanol-to-surfactant ratio, it partitions between the bulk-like core and the palisade layer. In the simulations, approximately 95 % of hexanol molecules reside in the micelles. This is in excellent agreement with the estimate of 91 % calculated for 12 wt % C12E10 solution based on Equation 3 in Table 2.

On the other hand, the order profiles of alkyl chains in pure C12E10 micelles in Figure 5 show maximal ordering slightly below the water/hydrocarbon interface followed by decrease in orientational order. The value of S_{CH} starts to increase again at distances larger than the core size. Inspection of the trajectories reveals that this results from surfactants being pulled by their headgroups into the water phase momentarily while still remaining anchored to the micelle by the tip of their alkyl tail. On the other hand, the ethylene groups in the ethoxylate chains show virtually no order, except near the micelle surface: the dip at the interface of the hydrocarbon core and the PEG head groups results from some ethoxylate chains partially wrapping around the micelle instead of being solvated. The increased order in the core, similarly to the alkyl chains, is due to the rest of the head group pulling the chain taut momentarily.

Hexanol solubilized solely to the palisade layer (at $\alpha = 0.25 - 0.5$) has no appreciable effect on the S_{CH} profiles. Solubilization of the hexanol into the micelle core and the resulting formation of an oil core (at $\alpha = 1.5 - 2.5$), as well as, the large amount of hexanol present at the interface seems, however, to decrease the overall orientational ordering of the alkyl chains in the micelle core. Curiously, the ordering of hexanol seems to increase towards the center of the core. This is because hexanol forms reverse structures, sometimes on its own and sometimes due to presence of residual water in the oil core. These reverse micellar structures of hexanol typically occupy the center of the oil core presumably because of steric repulsion from the ordered alkyl tails and confinement. While at first the formation of hexanol reverse micelles may seem curious, bulk octanol (both dry and wet) is suspected of presenting similar microheterogeneity response 69, 70.

To complete the discussion on the order parameter, Figure 6 presents the order parameter S_{CH} as a function of methylene group index which is the most traditional and the experimentally measurable form. The data shows that an increase in micelle size increases slightly the ordering of the alkyl tails. In the palisade layer, ethoxylate chains wrapping around the micelle, i.e., positive values of S_{CH}, become less common with increasing micelle size. This is presumably due to the increased shielding and crowdedness in larger micelles, which reduces the space and energetic benefit of chains wrapping the core. Presence of hexanol does not have a significant effect on the shape of the order parameter profile.

The calculated order parameter values are quite similar to those calculated from multi-field NMR relaxation experiments of C12E4 micellar systems 71, and are also consistent with published values from other micellar systems for the alkyl chain 72, 73. C12E4 micelles have been reported to exhibit higher order in the headgroups 74 than the data presented here for C12E10 micelles presumably because of the cylindrical shape of the former micelles 75. Additionally, in our analysis the order parameter director vector has not been corrected for micelle asymmetry.

Intermicellar interactions result, to a large part, from the palisade layer characteristics but the hydrocarbon core structure does influence the palisade layer. Because of the importance of the palisade layer in the intermicellar interactions, the local hydration conditions in it were characterized by calculating the average number of hydrogen bonds per ethoxylate group per chain. The data is presented in Figure 7. In brief, a hydration gradient is observed and this gradient becomes more pronounced for larger aggregates. The data shows that 5 – 6 of the innermost ethoxylate groups are dehydrated in comparison to the groups near the end of the chains. This is in agreement with the recent NMR results of Padia et al. 82, who observed that depending on the ethoxylate chain length 3 – 6 innermost groups show unique hydration, while the rest are similarly hydrated. Likewise, prior computer simulations 80 and experiments 24 on C12E7 micelles have indicated a two-shell structure for the palisade layer. In this, the palisade layer is proposed to have an inner layer, in which temperature-induced dehydration takes place, and an outer layer which is insensitive to temperature in its hydration response. Comparing the hydration of the small and large micelles in Figure 7, an analogous behaviour is observed: most of the size and shape induced dehydration occurs within the inner 5 – 6 ethoxylate groups. It should be noted that the exact behaviour depends on the reference micelle and the smallest analysed micelle $N_{agg} = 34$ appears as a slight data outlier. This is presumably because it is a border case between a premicelle and an actual micelle.

The data of Figure 7 also shows that reflecting its position in the micelle, hexanol bonds with the 2 – 3 innermost ethoxylate groups. However, because of the micelle surface roughness, the partial wrapping some headgroups around the micelle, as well as, hexanol diffusing in and out of the palisade layer, residual bonding of hexanol further along the ethoxylate headgroup is always present. In general, this residual bonding is, however, sufficiently insignificant not the affect the overall shape of the curves in Figure 7.

Figure 8 shows the mean number of hydrogen bonds per ethoxylate chain, the average end-to-end distance of the ethoxylate chain head group, and the average lifetime of water-ethoxylate hydrogen bonds for micelles of different size at different hexanol-to-surfactant ratios. The data reveals that an increase in micelle size coincides with the ethoxylate chain dehydration, slow-down of hydrogen bond dynamics, and extension of the ethoxylate chains. This behaviour results directly from the geometric properties of the polar-apolar interface: in a larger aggregate, surfactant molecules are densely packed. There is less space for water molecules to occupy which results in a slight dehydration of the chains and also isolation of water molecules, i.e. less competition for donor and acceptor sites.

On the other hand, presence of hexanol in the micelles consistently increases headgroup hydration while at the same time it decreases the hydrogen bond lifetime and head group end-to-end distance, i.e., makes the ethoxylate chains slightly more coiled. These effects result from hexanol having a spacer effect in
Fig. 5 Radial mass density $\rho$ (bottom panels) and order parameter $-S_{CH}$ (top panels) of different species at varying hexanol-to-surfactant ratios $\alpha$. The data points corresponding to bins with less than thousand samples are not plotted in the $S_{CH}$ profiles because of statistical uncertainty causing excessive scatter.

![Graph showing radial mass density and order parameter](image)

the micelles: hexanol residing between the surfactant molecules effectively moves the neighbouring chains further from one another, which facilitates ethoxylate access to water and enables more coiled conformations for the ethoxylate chains. However, the dehydration, hydrogen bond dynamics, and chain extension are much more sensitive to the size and shape of the micelle than to hexanol loading: only micelles at $\alpha > 1.5$ show significant deviation from the data points corresponding to pure C$_{12}$E$_{10}$ micelles.

**Discussion**

In this paper, the micellization response of C$_{12}$E$_{10}$ at varying amount of hexanol as additive was examined by DLS and cloud point experiments, as well as, molecular dynamics simulations. In the experiments, hexanol decreased the cloud point temperature of the C$_{12}$E$_{10}$ system and increased the effective hydrodynamic radius of the aggregates. Except for very high hexanol-to-surfactant ratios ($\alpha > 1.5$) where the $R_H$ response showed signs of also aggregate growth, this increase in $R_H$ was associated with attraction between the aggregates by comparison with the temperature response and literature. The molecular dynamics simulations, on the other hand, associated the presence of hexanol in the system, with increase of the head group hydration. Furthermore, micellar swelling due to an oil core formation was observed in the simulations at high hexanol loadings, while some indications of variability in the aggregate shape, i.e. presence of both spherical and elongated micelles was observed at low hexanol loading. The observed swelling could perhaps be related with the experimental $R_H$ data deviating from the pure temperature response at these high hexanol loadings.

In principle, self-assembly simulations such as here are able to predict the size and shape of the aggregates. However, the prediction suffers from insufficient system sizes joint with limited description time windows, and also imbalances in model parametrizations (model accuracy): in practise, the evolution of equilibrium micelle size and shape as a function of hexanol-to-surfactant ratio cannot be resolved from the self-assembly simulations. However, the simulations encompass a relatively large collection of individual micelles with varying size, shape and hexanol loading. This enables discussing the mechanism behind the experimentally observed cloud point depression and chang-
ing intermicellar interactions upon addition of hexanol. To this purpose, a simple but useful starting point is that water is a good solvent for ethoxylate chains in low temperature due to favourable ethoxylate-water interactions but turns to a bad solvent at high temperature. In other words, at high temperature ethoxylate chains become insoluble in water and clouding is observed. Adding a cosolvent, which retains favourable ethoxylate-water interactions but turns to a bad solvent for ethoxylate chains in low temperature due to lower degree of hydration of the ethoxylate chains. This is clearly in disagreement with the scheme outlined above.

To resolve the above discrepancy, the interactions with water in the system are next considered: while hydration increases, the lifetime of hydrogen bonds decreases (by up to 20%). This decrease results likely from increased water-water hydrogen bonding in the now somewhat less crowded palisade layer, and implies that water structure and consequently the average strength of ethoxylate-water hydrogen bonds decrease – possibly enough to compensate for the slight increase in the number of hydrogen bonds. This explanation, however, only works under conditions of constant micelle number density (i.e. constant aggregation number), since a change in aggregation number generally has as big or bigger influence to the headgroup hydration than hexanol addition. To illustrate the problem, simultaneous increase in aggregation number from 88 to 200 and in hexanol loading from 0 to 2.5 results in negligible loss of water-ethoxylate hydrogen bonds and a slight increase in hydrogen bond lifetimes (i.e. stronger bonds) – seemingly again at odds with the observation that hexanol decreases cloud point. Obviously the exact details of hydration and hydrogen bonding depend on the two micelles being compared, but the data indicates that changes in headgroup hydrogen bonding in the simulations cannot be easily correlated to changes in the experimental cloud point temperature in this system.

Intermicellar interactions, on the other hand, are much more straightforward to analyse in terms of micelle structure. In the spirit of the DLVO theory\textsuperscript{77–80}, the interactions of an alkyl ethoxy- late micelle can be thought of being composed of attractive van der Waals component and a repulsive steric component. Physically, steric repulsion in good solvent originates from two sources: volume restriction effect and osmotic effect. When the headgroup regions of two micelles overlap, some of the interfacial water is displaced and the local headgroup density increases. Volume restriction effect arises from this increased crowdedness and the resulting loss of configurational entropy. Osmotic repulsion, on the other hand, emerges from favourable solvent-headgroup interactions, which strive to reintroduce the displaced water molecules and dilute the headgroups back to the non-overlapping state.

In terms of micelle structure, hexanol appears to promote looser surfactant packing due to the spacer effect – in other words higher area per surfactant and less extended palisade layer (see data in Figures\textsuperscript{1} and \textsuperscript{3}). While probing the interactions directly for isolated micelles is not feasible, thermodynamic models of brush repulsion and experimental measurements on planar surfaces predict that increase in polymer concentration increases the extent and magnitude of the repulsion\textsuperscript{77–80}. This means that the steric repulsion occurs at larger separations and possibily overpowers completely the van der Waals attraction, see e.g.\textsuperscript{81–83}. On the other hand, at lower polymer concentration, the repulsion barrier is located nearer to the micelle core and a secondary minimum due to longer ranged attractive contributions can emerge. Thus, the spacer effect reducing the polymer density, and via that, the repulsive steric barrier by the head group, could actually be the origin of the change in interaction potential. A secondary contribution, could result from the surface of the micelle being covered with hydroxyl groups when the hexanol solubilizes at high

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure8.png}
\caption{The mean number of hydrogen bonds $<N_{HB}>$ per surfactant, the average water-$C_{12}E_{10}$ hydrogen bond lifetime $<\tau_{W}>$, and the mean end-to-end distance of ethoxylate chains $<\ell_{agg}>$ as a function of micelle aggregation number $N_{agg}$ at different hexanol-to-surfactant ratios $\alpha$. In the top panel, filled symbols correspond to the total number of hydrogen bonds and empty symbols to water-$C_{12}E_{10}$ bonds. Hydrogen bond lifetime has been normalized with the lifetime of water-water bonds. Dashed lines are provided as cues to the eye. Black squares ($\alpha = 0.00^\circ$) correspond to large, pure $C_{12}E_{10}$ micelles obtained from the hexanol self-assembly simulations by removal of hexanol molecules.}
\end{figure}
hexanol-to-surfactant ratio. This makes ethoxylate chains from different micelles subject to bridging due to ethoxylate-hexanol hydrogen bonding which could provide additional adhesive and enhance intermicellar attraction upon addition of hexanol.

Conclusions
In total, we have carried out a preliminary experimental mapping of aqueous hexanol/C12E10 solutions, and performed molecular dynamics simulations at varying hexanol loading. Experiments point towards increased micellar attractivity upon increased hexanol loading, with the possibility of aggregate growth at high hexanol-to-surfactant ratio. The simulations predict hexanol is solubilized into the palisade layer at low hexanol-to-surfactant ratio, while oil core forms at high hexanol-to-surfactant ratio. This makes ethoxylate chains from other cosurfactant-type n-alcohols, and alkyl ethoxylates.

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Conflict of interest
There are no conflicts to declare.

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