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Effect of 1-hexanol on C₁₂E₁₀ micelles: a molecular simulations and light scattering study†

Sampsa Vierros^a and Maria Sammalkorpi,^{*a}

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The micelles of non-ionic C₁₂E₁₀ 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-C₁₂E₁₀ 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 con-

financed 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 industries¹². 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, C₁₂E₅ has a cloud point of 32°C and exhibits strong mi-

^a Department of Chemistry and Materials Science, School of Chemical Engineering, Aalto University, P.O. Box 16100, FI-00076 Aalto, Finland.; E-mail: maria.sammalkorpi@aalto.fi

† Electronic Supplementary Information (ESI) available: The Electronic Supplementary Information consists of the DLS measurement data of the temperature dependence of *R_H* at varying *α* and additional final simulation snapshots (same initial composition but different starting configurations to those presented in Figure 3]. See DOI: 10.1039/b000000x/

cellar growth and morphological changes as temperature is increased towards the cloud point^{15,16}, whilst C₁₂E₈ has a cloud point of 75°C, and is believed to undergo only minor morphological changes as the cloud point is approached¹⁷.

To improve the performance and properties of the alkyl ethoxylate surfactant solutions, various additives such as alcohols^{18–20}, inorganic salts^{19,21}, and sugars²² 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^{23–29} but for non-ionic surfactants, with the notable exception of Pluronic^{30–34}, 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 ethoxylates¹⁸, sugar surfactants³⁵, and Triton X-100³⁶ exist.

Despite the vast amount of experimental work characterizing both pure C_iE_j 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 attractivity 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 C₁₂E₆ micelles to temperature and pressure^{37–39}, while Iyer et al. have studied the energetics of C₁₂E₄/C₁₂E₁₀ mixed micelles⁴⁰. 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 C₁₂E₁₀ micelles by light scattering experiments and molecular dynamics simulations in all-atom detail. We analyze in detail the structural response to variations in C₁₂E₁₀ and hexanol concentrations in this model system and associate the observations with changes in intermicellar attractivity. The surfactant C₁₂E₁₀ 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 C₁₂E₁₀ micelles have been studied experimentally significantly. The surfac-

tant C₁₂E₁₀ 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^{21,41–44}. While related surfactants with smaller headgroups exhibit considerable elongation and micellar growth when cloud point is approached (see e.g. Refs.^{13,14}), evidence suggests that the headgroup of C₁₂E₁₀ is sufficiently big to largely prevent such growth from taking place^{17,45–48}. However, reports on modest micelle elongation upon addition of potassium iodide and sugars exist^{21,22}. 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_{OXY+D} united-atom force field⁴⁹, SPC/E⁵⁰ explicit water model and GROMACS 5.0 simulation software. Long-range electrostatics were treated by the PME algorithm⁵¹ 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.⁵² ($\tau_T=0.5$ ps, $T_{\text{ref}}=298$ K) and the Parrinello-Rahman barostat⁵³ ($\tau_P=2$ ps, $P_{\text{ref}}=1$ bar). VMD was used for the visualization⁵⁴.

The micelles formed in 200 – 400 ns self-assembly simulations from random solutions of 200 C₁₂E₁₀ molecules (~12 wt % or ~200 mM C₁₂E₁₀ concentration) in pure water or with hexanol (HxOH) added at hexanol-to-surfactant molar ratios HxOH:C₁₂E₁₀ 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 C₁₂E₁₀ 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 % C₁₂E₁₀ concentration.

To obtain data unperturbed by micelle-micelle interactions, a set of micelles including their solvation shells (1 nm) were extracted from the simulations, resolvated 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 C₁₂E₁₀ 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 C₁₂E₁₀ 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_H , 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

$$e = 1 - \frac{I_1}{\langle I \rangle} \quad (1)$$

where I_1 is the smallest principal moment of inertia and $\langle I \rangle$ the mean inertia moment. The rod-to-disk parameter s is given by

$$s = \frac{I_3 - I_2}{I_3 - I_1} \quad (2)$$

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/N was evaluated by $A/N = 4\pi R_{hc}^2$ and $A/N = 4\pi R_{hc}^2 + 2\pi R_{hc}(L - 2R_{hc})$. Hydrodynamic radius R_H of the simulated micelles was estimated from the radius of gyration R_g according to⁵⁵

$$R_H = \sqrt{\frac{5}{3}} R_g \quad (3)$$

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 ⁵⁶

$$S_{ij} = \frac{1}{2} \langle 3 \cos \theta_i \cos \theta_j - \delta_{ij} \rangle \quad (4)$$

where θ_i 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 usual way for defining the local coordinate frame for united-atom chains⁵⁷. 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

$$S_{CH} = \frac{2}{3} S_{xx} + \frac{1}{3} S_{yy} \quad (5)$$

$S_{CH} = -0.5$ 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

Table 1 Simulated self-assembly systems. The table summarizes for each simulation the system name, the hexanol-to-surfactant molar ratios $[HxOH]:[C_{12}E_{10}]$, the numbers of $C_{12}E_{10}$ molecules $N_{C_{12}E_{10}}$, hexanol molecules N_{HxOH} , and water molecules N_{H_2O} , as well as, the total simulation time. Concentration of $C_{12}E_{10}$ is ~ 12 wt % except ~ 15 wt % in the simulation A+. The initial edge length of the cubic simulation box is 12 nm.

System name	$[HxOH]:[C_{12}E_{10}]$	$N_{C_{12}E_{10}}$	N_{HxOH}	N_{H_2O}	Time (ns)
A1	0.00	200	0	49565	400
A2	0.00	200	0	49589	200
A+	0.00	240	0	47958	200
B	0.25	200	50	49182	200
C1	0.50	200	100	48803	200
C2	0.50	200	100	48805	200
C3	0.50	200	100	49118	200
F	1.50	200	300	47292	200
D	2.50	200	500	45788	200

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. Decaethyleneglycol 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 MΩ-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 $1^\circ\text{C}/10$ 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 $C_{12}E_{10}$ ($12.7 \mu\text{M}$ ⁵⁸). Hence, micellization and aggregate formation can be expected.

The R_H data in Figure 1a 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 α^* , 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-

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_H response at α^* 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 α^* at which the R_H 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 α_{mic}^* can be estimated by solving the fraction of micellized hexanol f_{mic} from

$$K = \frac{x^{mic}}{x^{aq}} \quad (6)$$

$$x^{mic} = \frac{f_{mic} \cdot n_{HxOH}}{f_{mic} \cdot n_{HxOH} + n_{C_{12}E_{10}}} \quad (7)$$

$$x^{aq} = \frac{(1 - f_{mic}) \cdot n_{HxOH}}{(1 - f_{mic}) \cdot n_{HxOH} + n_{H_2O}} \quad (8)$$

Here x^{mic} and x^{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, α 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 α_{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, $\log K = 3.29^{59}$, 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_H increase in Figure 1a results partially from an increase of hexanol in the water solution: about half of

Table 2 DLS measured apparent hydrodynamic radius (R_H), the threshold $[HxOH]:[C_{12}E_{10}]$ molar ratio α for R_H increase onset, the calculated solubility-corrected $[HxOH]:[C_{12}E_{10}]$ threshold ratio α_{mic}^* , and fraction of micellized 1-hexanol f_{mic} at the different $C_{12}E_{10}$ wt % and the corresponding molar concentrations.

$[C_{12}E_{10}]$ (wt %)	$[C_{12}E_{10}]$ (mM)	R_H (nm)	α^* (mol/mol)	α_{mic}^* (mol/mol)	f_{mic} (%)
1.0	16.2	3.92	2.15	1.19	55
2.2	34.4	3.65	1.30	0.89	68
12.1	192	3.04	0.35	0.32	91

the difference between α^* at the different concentrations can be attributed to the water solubility of hexanol.

Three principal effects can explain the data in Figure 1, and the observed increase in the apparent R_H . First, the swelling of micelles due to hexanol solubilization into the micelles would result in an increase of micelle size, and apparent R_H ; in this case, the observed threshold would correspond to onset of swelling. Second, cosurfactant solubilization into the palisade layer of the micelle may influence the packing of surfactant molecules sufficiently to cause anisotropic micellar growth; the observed threshold would correspond to onset of the growth. Third, changes in the $C_{12}E_{10}$ headgroup hydration or conformation influence the intermicellar interactions, i.e. increase or decrease of barriers. Especially in concentrated solutions, intermicellar interaction strength reflects on the measured apparent R_H value. In practise, sticky micelles appear larger than the more repulsive ones of the same actual size. In this case, the observed threshold would be a change in the intermicellar attraction.

Obviously these three effects are rather difficult to distinguish via mere apparent R_H considerations as all lead to an increase of the measured R_H . However, a literature survey on the thermal response of $C_{12}E_{10}$ micelles provides useful insight. Danino et al. have shown via cryo-transmission electron micrographs that $C_{12}E_8$ micelles remain spherical up to temperatures close to cloud point⁴⁶. Furthermore, neutron scattering^{17,45} and rheological experiments¹⁷, as well as, time-resolved fluorescence spectroscopy⁴⁷ and gradient NMR⁴⁸ support the view that alkyl ethoxylates with large headgroups show negligible asymmetric micellar growth with temperature. Instead, most of the apparent growth can be explained in terms of increased attraction between the micelles, micellar collisions and cluster formation. As $C_{12}E_{10}$ is a member of this class, we deduce that any observed thermotropic growth is likely to correspond to increased intermicellar attraction. On the other hand, deviation from the temperature induced R_H response upon addition of hexanol indicates that another kind of origin, i.e. swelling or asymmetric growth, could be involved. To resolve whether this is the case, next the thermal response and the hexanol induced changes in the two data sets are compared and isolated from each other.

The insert of Figure 2 shows the evolution of R_H as a function of temperature. The data shows that R_H of pure $C_{12}E_{10}$ solutions remain nearly constant upto $\sim 35^\circ\text{C}$, after which R_H starts to increase due to the temperature increase. This response is typical of C_iE_j surfactants, and the measured apparent R_H increase has been attributed to the onset of intermicellar attraction^{47,60–62} resulting from dehydration of the ethoxylate chains. Samples con-

Fig. 1 a) DLS measured hydrodynamic radius R_H and b) the corresponding cloud point temperatures T_{CP} as a function of hexanol-to-surfactant molar ratio α at 25°C for $C_{12}E_{10}$ solutions at different concentrations. In panel a), to prevent overlap, the R_H curves of 2 and 12 wt % solutions have been shifted by 2 nm and 4 nm up in the y-direction, respectively.

taining hexanol show similar overall behaviour to pure $C_{12}E_{10}$ solution, but the onset of temperature induced increase in R_H shifts to progressively lower temperatures (see Electronic Supplementary Information Figure S1).

In Figure 2, to quantify the difference between thermal and hexanol-induced response, the actual R_H measured at 25°C and varying hexanol-to-surfactant ratio is compared to R_H of pure $C_{12}E_{10}$ solution sampled at temperature $(25^\circ\text{C} + \Delta T_{CP}(\alpha))$, where $\Delta T_{CP}(\alpha)$ is the change in cloud point at a given hexanol-to-surfactant ratio α . In effect, this operation mimics the observed hexanol-induced shift in the R_H vs T curves (Figure S1) at a fixed temperature of 25°C under the assumptions that the shape of the curve does not change and the shift in temperature equals the change in cloud point $\Delta T_{CP}(\alpha)$. With this shift, the two data sets are practically superposed with the exception of the highest α values. Together with the literature survey above, this is a strong indication that the apparent increase in R_H is dominated by a change in the intermicellar interaction potential. Curiously, the two data sets diverge at $\alpha \geq 1.5 - 2$. This implies a possibility of swollen micelles or asymmetric growth at elevated hexanol concentrations, although literature data on the behaviour of pure alkyl ethoxylates does not support the latter¹⁷. As said, the swelling would correspond to hexanol solubilization into the micelles: For comparison, in SDS micelles, 1-hexanol and 1-heptanol oil cores develop at molar ratios $1.7 - 2$ ^{63,64} at 40 mM concentration.

In summary, this experiments based initial charting of the influence of hexanol on the $C_{12}E_{10}$ solution suggests that hexanol has a

Fig. 2 Comparison of R_H of $C_{12}E_{10}$ solution with varying α measured at 25°C (actual data) and the R_H of pure $C_{12}E_{10}$ solution sampled at temperature $(25^\circ\text{C} + \Delta T_{CP}(\alpha))$ and plotted here at the α corresponding to the shift (shifted data). The insert shows the temperature dependence of R_H for pure $C_{12}E_{10}$ solutions. For the temperature dependence of R_H at varying α , see Figure S1 in the Electronic Supplementary Information.

strong influence on the intermicellar interactions but also points toward the aggregate swelling at high hexanol-to-surfactant ratio. 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 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 125⁴¹⁻⁴³, hydrodynamic radii between 2.9 nm and 4.0 nm^{21,41,44} and a core radius of 1.7 nm⁴¹ 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 e 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 α . 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 ($\alpha = 0.00^*$) 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 ~ 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 α appears to promote spherical aggregate shape and is also associated with a substantial increase in the area per surfactant a . 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 prior 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^{65,66}. We note, however, that prolate micelles with such a low axial ratio as the ones present in the simulations have (2.1 – 3.4) cannot be discriminated from spherical micelles in the existing electron micrographs⁴⁶ 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^{16,22}. 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^{67,68}. 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 6 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 methylene 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 more 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 C₁₂E₅ micellar systems⁷¹, and are also consistent with published values from other micellar systems for the alkyl chain^{72,73}. C₁₂E₅ micelles have been reported to exhibit higher order in the headgroups⁷¹ than the data presented here for C₁₂E₁₀ micelles pre-

sumably because of the cylindrical shape of the former micelles¹⁵. 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.⁶⁷ 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 simulations³⁹ and experiments⁷⁴ on C₁₂E_j 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 to 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 ρ (bottom panels) and order parameter $-S_{CH}$ (top panels) of different species at varying hexanol-to-surfactant ratios α . 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.

Fig. 6 Order parameter $-S_{CH}$ of pure C₁₂E₁₀ micelles of different aggregation numbers as a function of methylene group CH₂ index. The skeletal formula at the top shows the numbering of the C₁₂E₁₀ molecule methylene and ethoxylate oxygen groups (black and red, respectively).

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 $\alpha \geq 1.5$ show significant deviation from the data points corresponding to pure C₁₂E₁₀ micelles.

Discussion

In this paper, the micellization response of C₁₂E₁₀ 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 C₁₂E₁₀ system and increased the effective hydrodynamic radius of the aggregates. Except for very high hexanol-to-surfactant ratios ($\alpha \geq 1.5$) 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, and the solubilization response of hexanol into the micelles, 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 vari-

Fig. 7 Mean number of hydrogen bonds N_{HB} per ethoxylate group for water as a function of aggregation number, the normalized life time of the bonds τ/τ_w , and the number of hydrogen bonds per ethoxylate group for hexanol as a function of hexanol-to-surfactant ratio α . The ethoxylate group indexing starts from the alkyl tail, i.e., ethoxylate group 1 corresponds to the ethoxylate oxygen nearest to the core (see Figure 6).

ety 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-

Fig. 8 The mean number of hydrogen bonds $\langle N_{HB} \rangle$ per surfactant, the average water- $C_{12}E_{10}$ hydrogen bond lifetime $\langle \tau/\tau_W \rangle$, and the mean end-to-end distance of ethoxylate chains $\langle l_{head} \rangle$ as a function of micelle aggregation number N_{agg} at different hexanol-to-surfactant ratios α . 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 life time has been normalized with the lifetime of water-water bonds. Dashed lines are provided as cues to the eye. Black squares ($\alpha = 0.00^*$) correspond to large, pure $C_{12}E_{10}$ micelles obtained from the hexanol self-assembly simulations by removal of hexanol molecules.

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 and cosolvent-water interactions across a wide temperature range, generally increases the cloud point. Similarly, a cosurfactant insoluble in water, but capable of interacting favourably with ethoxylate chains, competes with water molecules making the surfactant less soluble, and generally lowering the cloud point. Hexanol belongs to the latter group. To assess, whether this scenario really explains the depression of cloud point, it is instructive to assess the $C_{12}E_{10}$ headgroup hydration data: micelle size and hexanol loading can be identified as the main factors affecting the headgroup hydration in the data. The hydrogen bond profiles show that, indeed, hexanol competes with water to a certain extent over hydrogen bonds with ethoxylate chains. This competition could lower the cloud point as discussed above. However, the data also shows quite clearly that for micelles with similar sizes the hydration of ethoxylate chains actually increases slightly because the hexanol solvated in the palisade layer has a spacer effect, i.e. the hexanol molecules sit between the surfactant molecules and open up the headgroup region resulting in

higher 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 upto 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 straight forward to analyse in terms of micelle structure. In the spirit of the DLVO theory^{75,76}, the interactions of an alkyl ethoxylate 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 4 and 8). 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^{77–80}. This means that the steric repulsion occurs at larger separations and possibly overpowers completely the van der Waals attraction, see e.g.^{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

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. Overall, hexanol increases hydration of the headgroups and water dynamics at the palisade layer through hexanol decreasing the effective crowdedness of the surfactant/water interface. As the simulations include a range of micelle sizes, morphologies and alcohol loadings, they provide a useful molecular-level reference point for further work on solute-surfactant and surfactant-water interactions. The findings are likely to hold also for 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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