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**MASTER'S DEGREE FINAL PROJECT**

**COARSE-GRAINED MEAN FIELD SIMULATIONS OF TRIBLOCK COPOLYMER SYSTEMS**

**The Effect of Flexibility on the Micellization behavior**

**Supervised by Dr. Allan Mackie**

**MASTER'S DEGREE IN NANOSCIENCE, MATERIALS AND PROCESSES**

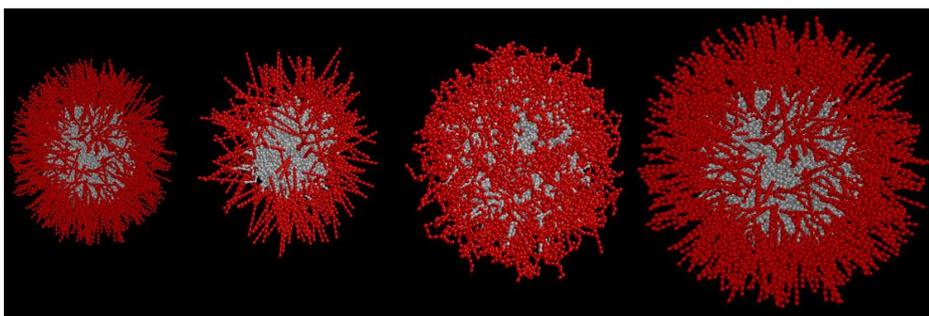


UNIVERSITAT ROVIRA I VIRGILI

**Tarragona 2017**

**COARSE-GRAINED MEAN FIELD SIMULATIONS OF TRIBLOCK COPOLYMER SYSTEMS****The Effect of Flexibility on the Micellization behavior.*****Pantelidou Maria****Master Program in Nanoscience, Material and Processes, 2016-2017*Email: [mapantel@physics.auth.gr](mailto:mapantel@physics.auth.gr)Supervisor: **Dr. Allan Mackie***Department of Chemical Engineering. University Rovira i Virgili.**Campus Sescelades, Avinguda dels Paisos Catalans 26. 43007 Tarragona Spain.***ABSTRACT**

Micelles appear when surfactants in an aqueous media, start to self-assemble into aggregates above a certain concentration. This physical mechanism of the micelle formation is key to developing new intelligent materials having a strong impact in selective drug delivery, tissue repair, molecular recognition, and many others. In this work, Single Chain



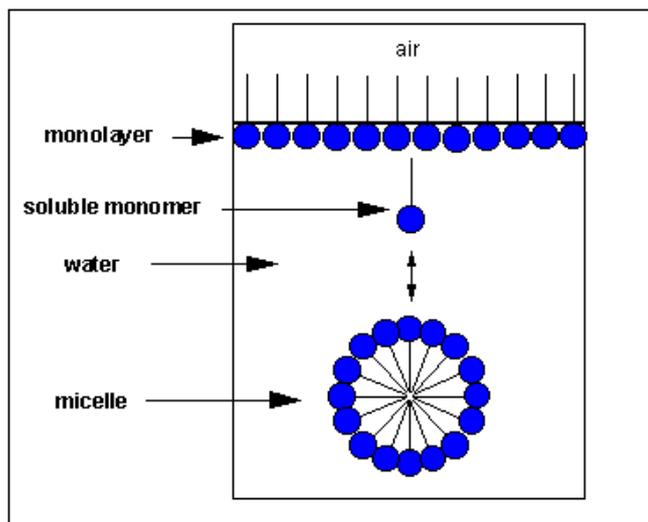
Mean Field Theory (SCMF) is used as a simulation method in order to study the effect of changing the flexibility of surfactant chain in the micellization behavior. Critical Micelle Concentration (CMC), aggregation number and micellar size and architecture were examined by using a coarse-grained model for the L44 Pluronic, a trademarked type of triblock copolymer in water at 37 °C. We found that increasing the chain stiffness, the CMC decreases. In addition, in agreement with previous experimental and theoretical studies we observed a significant dependence between the flexibility of the surfactant chain and the aggregation number. On increasing chain stiffness the aggregation number is increased strongly. Furthermore, a structural analysis based on surfactant heads and tail fraction distributions, as well as solvent fraction distribution, show us that stiffening the whole chain the resulting micellar aggregate is larger than an aggregate composed by flexible chains, without deviations from spherical symmetry.

**INTRODUCTION**

The term amphiphilic refers to those compounds containing both, molecules that have affinity for water and molecules that have affinity for oil. In particular, we can refer to the so-called surfactants, whose molecules consist of one hydrophobic head and one hydrophilic tail which can be linear or branched.

Due to this amphiphilic nature, surfactants have a very interesting behavior when they are surrounded by a solvent (e.g. water). For example, surfactants in a solution, tend to be located at the air/solution interface with the hydrophobic head group in the solution and the hydrophilic tail in the air, forming a layer of surfactant which reduces the surface tension of the solution.

As the surfactant concentration in solution is increased, the number of the hydrophobic tails is increased too resulting in an increase of the free energy of the system (Maibaum, Dinner, and Chandler 2004). To prevent and to reduce the increase of free energy, surfactants start to self-associate in micelles which can change shape and size continuously, above a specific amount of concentrated surfactants which is called Critical Micelle Concentration (CMC) (Figure 1.).



**Figure 1.** Micellization process. Surfactants in water start to self-associate into micelles above a certain concentration. Hydrophilic heads form an outer shell in contact with water, while hydrophobic tails are sequestered in the interior.

This physical mechanism of micelles formation, made the surfactants to gain the interest of several industrial, technological and research processes including the improving of solubility, stability and targeting of nanoparticles by coating surfactants on its surface. Also, surfactants are very interesting in the cleaning industry where the Critical micellar Concentration (CMC) is related to the concentration at which solubilization in the soil removal process occurs. They are also used as templates for the synthesis of mesoporous materials, in waste water treatments for the separation of toxic ingredients and in medicine where surfactants can be used as drug delivery vehicles.

Surfactants whose molecular sizes are 10-100 times bigger than the common surfactants are the so-called block copolymers. There are many types of these block copolymers such as diblock or triblock copolymers. Poly (ethylene oxide)-poly (propylene oxide)-poly (ethylene oxide) molecules constitute a type of linear triblock nonionic copolymer surfactant commercially available as Pluronics. Pluronics consist

of a central hydrophobic poly (propylene oxide) (PPO) chain connected to two hydrophilic poly (ethylene oxide) (PEO) chains. At high concentrations of these surfactants, above the CMC, molecules start to self-assemble into micelles and later, as the concentration increases, into worm-like aggregates (Cates and Candau 1990).

The CMC of many surfactants including Pluronics, has been determined experimentally through a number of techniques including light scattering, surface tension, spectrophotometry, nuclear magnetic resonance, capillary electrophoresis and fluorimetry. For example (Nolan et al. 1997) have been determined structural properties of micelles formed by different Pluronic types, by using both dynamic and static light scattering technique. Also, (Steytler 2000) have used the small-angle neutron scattering (SANS) method, in order to investigate the temperature dependence of the micellar structure, which is formed by the poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) Pluronic L64 block copolymer in aqueous ( $D_2O$ ) solution. Spectrophotometry, isothermal titration calorimetry and dynamic light scattering method have been used from (Naskar, Ghosh, and Moulik 2012) for the determination of the CMC, the critical micelle temperature (CMT) and the cloud point (CP), for Pluronics L44. However, those experiments have faced issues in reproducibility, speed and cost.

On the other hand, concerning theoretical methods, computer simulations are able to provide a more complete understanding at a microscopic level, thermodynamically dynamic properties including the critical micellar concentration, the aggregation number, the micellar aggregates shape etc. in equilibrium in a fast and low cost manner. The most relevant simulation methods are the Monte Carlo (MC) simulations (Engineering 1997), where the equilibrium of the system is reached by a series of random moves, the Molecular Dynamics (MD) simulations (Levine et al. 2011) which are based on the classical laws of motion (Newton's second law) from where we can study the equilibrium and the Brownian dynamics (Hafezi and Sharif 2015) which includes frictional and random forces in Newton's equations. However only a short window of time can be reached by these types of simulation due to the large amount of computation time needed.

Another methods arising from the mean field theories are also able to predict dynamic properties in a wide range of surfactant systems. Specifically, the free energy of the system, which is written in the terms of sampling chains representing the surfactants, is minimized in order to reach the equilibrium. The Self-Consistent Field (SCF) and the Single-Chain Mean Field (SCMF) theories have been used to study block copolymer systems due to the fact that they are able to predict dynamic properties in equilibrium. In contrast SCMF method can take into account self-avoiding conformations leading in a more realistic model of block copolymer surfactant systems (Garc??a Daza, Colville, and Mackie 2015b), (Garc??a Daza, Colville, and Mackie 2015a).

Most of the existing studies have been focused on the effect of changing the surfactant chain length. For example (Maibaum, Dinner, and Chandler 2004) presented a theory for micelle assembly. Their theoretical predictions for the temperature and surfactant chain length dependence of the CMC for nonionic surfactants were in agreement with experimental data. In addition, (Bhattacharya and Mahanti 2001), showed that for amphiphiles of different chain lengths and different head-to-tail length ratios the CMC decreases on increasing the chain length.

In our study we are focusing on the effect of changing the flexibility of surfactant chain. The chain flexibility controls the architecture of chain. More specific, changes in chemical composition of surfactant molecules have impact on the intramolecular interactions which will possibly affect the bending ability of the backbone and as a consequence they will affect the micellization behavior and the final structure-size of micelle. For example, (Tsige, Leuty, and Bedard 2009) studied the microphase separation of symmetric diblock copolymers with different block stiffness and different block chain lengths using coarse- grained molecular dynamics simulations.

In this work, a series of simulations within the SCMF theory have been used for the L44, a type of Pluronics which has the physical properties obtained in the table 1. Systematic changes in the flexibility of the whole chain and independently, either in the hydrophobic or in the hydrophilic group of the chain have been introduced in order to provide predictions of the CMCs together with the corresponding aggregation numbers and micellar profiles.

Polymer	Molecular Weight	Number of PO units	Number of EO units
L44	2200	23	20

Table 1. Physical properties of L44 Pluronic Block copolymer.

## Model and Simulation Method

### Simulation Method

**Single-Chain Mean Field Theory:** This theory is based on the reduction of many-bodies problem to one-body problem. Therefore, this theory considers a single central chain, that belongs to a set of conformations  $\{\gamma\}$  representing the surfactant, in order to study its interactions with the system (solvent and other surfactants). Specifically, these interactions refer to the **a) Intramolecular interactions**, which are determined in an exact way and to the **b) Intermolecular interactions** with the solvent and the other surfactant chains, which are taken within a mean-field approximation and they are determined by the probability distribution function of the chain conformations,  $P[\alpha]$  and the distribution of the solvent molecules into the aggregate, by the minimization of the aggregate's total free energy. Once the probability distribution function is known, any thermodynamic property of micellar aggregate can be calculated.

The aggregate's total free energy is given by:

$$\langle F \rangle = \langle E \rangle - T \langle S \rangle \quad (1)$$

Where the energy in this system is given in terms of averaged energetic values of configurations of the surfactant,  $\{\gamma\}$ , weighted by its individual probabilities,  $P[\gamma]$ :

$$\langle E \rangle = N \int P[\gamma] (U_{intra}[\gamma] + U_{inter}[\gamma]) d\gamma \quad (2)$$

Where  $U_{intra}[\gamma]$  is the exact internal energy of conformation  $\gamma$  and  $U_{inter}[\gamma]$  refers to the intermolecular energy and according to the above explanation is equal to:

$$U_{inter}[\gamma] = \frac{N-1}{2} \int P[\beta] U_{inter}[\gamma, \beta, \vec{r}] d\vec{r} d\beta + \int c_s(\vec{r}) U_{inter}[\gamma, \vec{r}] d\vec{r} \quad (3)$$

The first term of the equation (3) refers to the intermolecular surfactant interactions of the conformation  $\gamma$  with the remaining N-1 surfactants in the system, where the  $P[\beta]$  corresponds to the probability distribution function of the conformation  $\beta$  and the  $U_{inter}[\gamma, \vec{r}] = \sum_{i,j} \varepsilon_{i,j} \Phi_i(\gamma, \vec{r}) c_i(\beta, \vec{r})$ . The interaction parameters,  $\varepsilon_{i,j}$  together with the interaction volume,  $\Phi_i(\gamma, \vec{r}) d\vec{r}$  (volume in which the configuration  $\gamma$  can interact with the remaining conformations  $\{\beta\}$  at  $\vec{r}$ ) and the corresponding concentration,  $c_i(\beta, \vec{r})$ , make up the coarse-grained model.

The second term of the equation (3) refers to the surfactant interaction with the solvent through its concentration field  $c_s(\vec{r})$  at  $\vec{r}$ .  $U_{inter}[\gamma, \vec{r}] = \sum_i \varepsilon_{i,s} \Phi_i(\gamma, \vec{r})$ , where  $\varepsilon_{i,s}$  is the surfactant-solvent interaction parameter.

We assume that all regions of the physical space are occupied by solvent or surfactant molecules by means of the corresponding volume fractions. This aspect is given by:

$$\varphi_s(\vec{r}) + N \sum_i \langle \varphi_i^{exc}(\vec{r}) \rangle = 1 \quad (4)$$

Where the  $\varphi_i^{exc}(\vec{r})$  is the excluded volume fraction which is the total physical volume fraction of species  $i$  of conformation  $\gamma$  at  $\vec{r}$  that cannot be accessed by solvent or other surfactant molecules.

The average excluded-volume fraction of the surfactant, is given by:

$$\langle \varphi_i^{exc}(\vec{r}) \rangle = \int P[\gamma] \varphi_i^{exc}(\gamma, \vec{r}) d\gamma \quad (5)$$

And the concentration fields of the surfactant monomers, is given by:

$$\langle c_i(\vec{r}) \rangle = \int P[\gamma] c_i(\gamma, \vec{r}) d\gamma \quad (6)$$

The entropy of the system consists of the conformational entropy of the chains:

$$S_1 = -kN \int P[\gamma] \log P[\gamma] d\gamma \quad (7)$$

And the translational entropy of the solvent molecules:

$$S_2 = -k \int c_s(\vec{r}) \log \varphi_s(\vec{r}) d\vec{r} \quad (8)$$

If we sum up the equations (1), (2), ((7), (8), we obtain the aggregate's total free energy:

$$F = N \int P[\gamma] (U_{intra}(\gamma) + U_{inter}(\gamma)) d\gamma + kT(N \int P[\gamma] \log P[\gamma] d\gamma + \int c_s(\vec{r}) \log \varphi_s(\vec{r}) d\vec{r}) \quad (9)$$

Where  $k$  is the Boltzmann's constant and  $T$  the temperature of the system.

The individual probabilities of the conformations  $P[\gamma]$  in equilibrium are found from the minimizing of the equation (9):

$$\frac{\delta F(P[\gamma])}{\delta P[\gamma]} = 0 \quad (10)$$

Subject to the volume-filling constraint in equation (4), by the way of the Lagrange multiplier,  $\lambda(\vec{r})$ . This gives:

$$P[\gamma] = \frac{1}{Q} e^{-\mathcal{H}_N[\gamma]/kT} \quad (11)$$

Where Q is the normalization factor which ensures that:

$$\int P[\gamma] d\gamma = 1 \quad (12)$$

And  $\mathcal{H}_N(\gamma)$  is the Hamiltonian given by:

$$\begin{aligned} (13) \\ \mathcal{H}_N(\gamma) \approx U_{intra}(\gamma) \\ + (N-1) \int \sum_{i,j} \epsilon_{i,j} \Phi_i(\gamma, \vec{r}) < c_j(\vec{r}) > d\vec{r} \\ + \int \sum_i \epsilon_{i,s} \Phi_i(\gamma, \vec{r}) c_s(\vec{r}) d\vec{r} \\ - kT \int \frac{\log \phi_s(\vec{r})}{v_s} \sum_i \phi_i^{exc}(\gamma, \vec{r}) d\vec{r} \end{aligned}$$

Where  $v_s$  is the molar volume of the solvent.

This set of nonlinear equations (4)-(6), (11), (13) except from the individual probabilities,  $P[\gamma]$ , determination, can give us the equilibrium properties for aggregates of size N and also the densities and the concentrations.

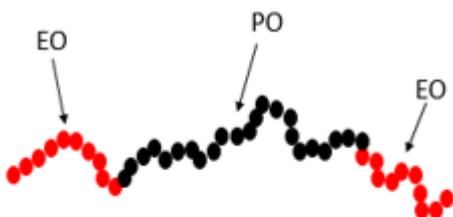


Figure 2. Coarse-grained model for Pluronic L44 EO10PO23EO10. Red beads represent the Hydrophilic head group ( $CH_2CH_2O$ ), while black beads represent the Hydrophobic tail groups ( $(CH_2CH_2)_3CH_2O$ ).

## Model

The first step of the SCMF calculations is the definition of a coarse-grained model of a molecule and its interactions with the mean fields. To do so, we have used a coarse-grained model for Pluronic L44 EO<sub>10</sub>PO<sub>23</sub>EO<sub>10</sub> in water at a constant temperature of 37 °C from a previous work. (figure 2.) (García Daza, Colville, and Mackie 2015b) , . This model is a linear chain consists of two kinds of beads with the same diameter  $\sigma$ . The first one represents the hydrophilic group ( $CH_2CH_2O$ ) and the second one represents the hydrophobic group ( $(CH_2CH_2)_3CH_2O$ )(Figure 2.). More specific, we can see the coarse-grained structural and energy specifications of our model in table 2.

Diameter ( $\sigma$ )	1.0
Bond length ( $\sigma$ )	1.0
Interaction radius ( $\sigma$ )	1.62
EO-PO Interaction parameter ( $\chi_{EO,PO}$ )	0.006
EO-S Interaction parameter ( $\chi_{EO,S}$ )	0.5
PO-S Interaction parameter ( $\chi_{O,S}$ )	2.1

Table 2. Coarse-Grained Structural and Energy Specifications.

## Flexibility of the chain

The Kuhn segment length  $l_k$  is a measure for the stiffness of the polymer chain(Aharoni 1983). More specific, a real polymer chain is considered as a collection of N Kuhn segments, each with a Kuhn length  $l_k$ . Each segment in a freely jointed chain can randomly orient in any direction without the influence of any forces, independent of the directions taken by other segments. In other words, the polymer chain is described by a random walk with a contour length:

$$L = N \cdot l_k \quad (14)$$

In a previous work, (García Daza, Colville, and Mackie 2015b), where the same model had been used, the chain stiffness had been included by using rigid sections of four consecutive monomers in the case of PO and five monomers in the case of EO species.

For our hypothetical study on investigating the effect of stiffness in micelles formation, we have changed arbitrarily the number of Kuhn segments. For

example, for a total flexible chain we have used 2 consecutive monomers in case of PO and 2 monomers in the case of EO species. On the other hand, for a total rigid chain we have used 10 consecutive monomers in case of PO and 23 monomers in the case of EO species (table 3.).

### Simulation details

In order to check that the box size is correct and the number of sampling chains is sufficient, we ran a series of simulations with different box sizes and different number of conformations  $\{\gamma\}$ . The dimensions of those boxes were between 30x30x30 and 60x60x60 and the number of sampling chains from 1 thousand to 100 million. By checking the behavior of the standard chemical potential with respect to the aggregation number in SCMF equations (N) and the aggregation number of the micelle when excluding the surfactants in the bulk ( $N_c$ ), we determined that the best behavior obtained was for boxes with dimensions: 40x40x40 for total rigid chain, 45x45x45 for medium flexibility chains and 50x50x50 for total flexible chain. In addition, a sufficient number of conformations  $\{\gamma\}$  was 10 million. The simulation was run on 12-core Intel machines, 24-core and 32-core AMD machines with RAM memory of 64, 32 and 128GB, respectively.

## Results and Discussion

In this work, the micellization behavior and the physical properties of the EO<sub>10</sub>PO<sub>23</sub>EO<sub>10</sub> Pluronic (Molar Weight=2200) were studied at a constant temperature (T=37 °C) while systematic changes in the flexibility of the whole chain and independently either in the hydrophobic tail or in hydrophilic head occur. First, we studied how the chain flexibility affects the CMC and the aggregation number and second we analyzed more deeply the effect in micellar size and architecture.

In the first case, in order to calculate the Critical Micelle Concentration (CMC), we need to determine the minimum Standard Chemical Potential difference for each case of chain flexibility. To do so, we plotted the Standard Chemical Potential differences, obtained by the SCMF theory, versus the aggregation number of the micelle when excluding the surfactants in the bulk ( $N_c$ ). (Figure 3.).

In addition, through this figure, we are able to obtain the preferred aggregation number for each case, due to the fact that the preferred aggregation number corresponds to the minimum of the chemical potential difference.

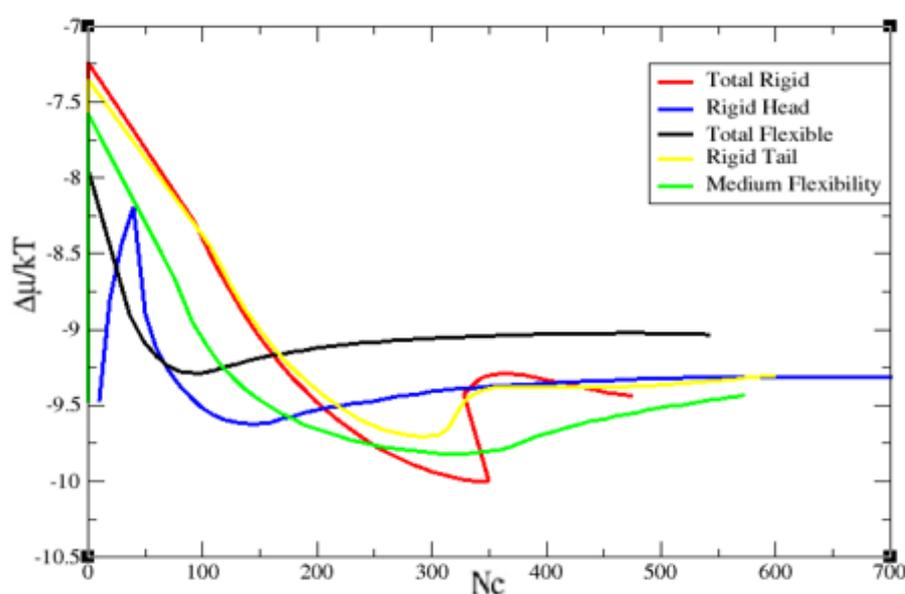


Figure 3. Standard chemical potential differences ( $\frac{\mu_i^0 - \mu_i^1}{kT}$ ) versus the aggregation number of micelles, when excluding the surfactants in the bulk  $N_c$ , for Pluronic of L44 type with different surfactant chain flexibility.

As I mentioned, the CMC value in mole fraction, X, is taken based on the minimum of standard chemical potential differences according to the following equation:

$$CMC_X = X = e^{(\frac{\Delta\mu}{kT})_{min}} \quad (14)$$

Furthermore, the CMC in mole fraction, X, is related to the CMC in (mol/L) from the following relationship:

$$CMC_{(\frac{mol}{L})} = \frac{1}{V_M + V_S(\frac{1}{X} - 1)} \quad (15)$$

Where  $V_S$  and  $V_M$  are the molar volume of the solvent (water=0.018 L/mol) and the molar volume of the surfactant (Pluronic L44=2.2 L/mol) respectively (Kozlov et al. 2000).

The  $CMC_{sim}$ , as well as the preferred aggregation number results appear in the table 3.

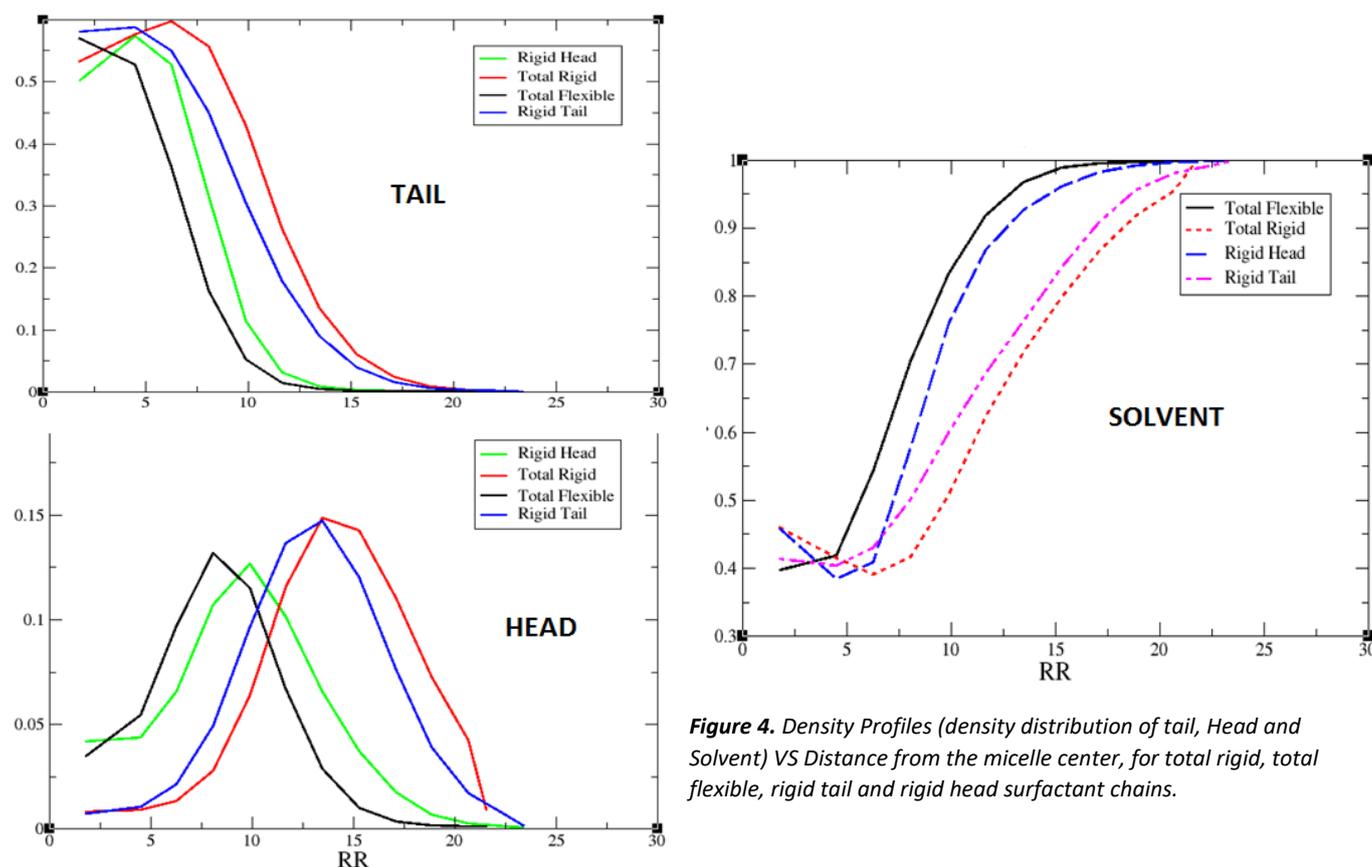
We observe that in a given temperature T, the CMC value is smaller for stiffer chains, while the aggregation number is bigger. Contrariwise, when the surfactant chain is flexible, the CMC value is higher, while the aggregation number is lower. This result, is in agreement with previous theoretical studies. For example (Firetto, Floriane, and Panagiotopoulos 2006) have been found that increasing the chain stiffness, CMC value decreases while the average micelle size increases.

Now, stiffening only the tails leads to a more negative free energy than stiffening the heads. This has a consequence in significant change in aggregation number, which is much higher for rigid tails than for rigid heads. On the contrary, the CMC value is not much sensitive. Overall, the largest aggregation numbers are obtained when both head and tail groups are rigid. Changing only the head or the tail flexibility, we obtain slightly larger aggregates for chains with stiff tails.

Now, In order to analyze deeply these results, we need to study the distribution of heads, tails and solvent. To do so, we plotted the density profiles of micelles (surfactant head, surfactant tail and solvent) versus the distance from the micellar center, for each case of stiffness. (Figure 4.).

Case of study	I Kuhn (H)	I Kuhn (T)	N	Nc (simulation)	$\Delta\mu/kT$	CMC simulation (mol/L)
Total Flexible	2	2	100	91	-9.293	$5.05 \cdot 10^{-3}$
Medium	5	12	340	324	-9.819	$3 \cdot 10^{-3}$
Random	4	3	150	142	-9.47	$4.2 \cdot 10^{-3}$
Total Rigid	10	23	390	350	-10.006	$2.48 \cdot 10^{-3}$
Flexible Tail and Rigid Head	10	2	150	141	-9.626	$3.63 \cdot 10^{-3}$
Flexible Head and Rigid Tail	2	23	300	287	-9.708	$3.34 \cdot 10^{-3}$

**Table 3.** Micellization behavior of L44 Pluronic block copolymer as a function of the chain flexibility. From the left to the right, the flexibility of the chain, the number of Kuhn segments for the head and the tail, the aggregation number in the SCMF equations, the preferred aggregation number of the micelle when excluding the surfactants in the bulk, the minimum standard chemical potential differences and the Critical Micelle Concentration of our simulations.



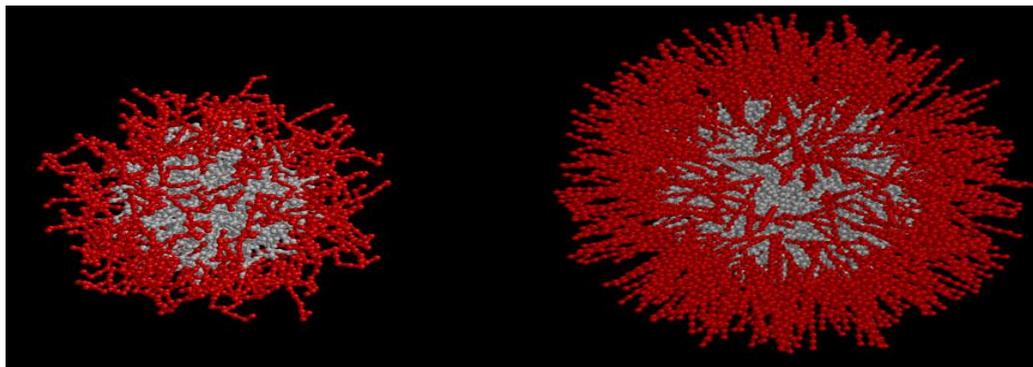
**Figure 4.** Density Profiles (density distribution of tail, Head and Solvent) VS Distance from the micelle center, for total rigid, total flexible, rigid tail and rigid head surfactant chains.

Generally, in all flexibility cases, at small distances from the micellar center, the tail distribution function is close to a maximum value of 0,6 and the head and the solvent values are close to zero. At medium distances the tail distribution function decreases while the head and solvent increases. At larger distances, the head as well as the tail concentrations drop to zero while the solvent concentration reaches a maximum value close to 1, means that finally at large distances from the center, only solvent molecules are present.

Independently, for each case of chain flexibility, we obtained that at small distances from the micellar core, the tails are more crowded and much greater for stiffer surfactant chains than for flexible. This observation leads to the larger aggregation number for stiffer surfactant chains.

With respect to the solvent distribution function, the maximum related to micellar size. We can observe from the third plot that, the maximum value of 1, where only the solvent molecules are present, is reached faster from aggregates constitute of flexible chains. As a consequence the size of micelle is larger when is composed of stiffer surfactant chains.

In Figure 5. are presented the schematic diagrams of the micelles composed by surfactant chains of twenty head units and twenty-three tail units with different chain flexibilities (total flexible and total rigid) given in table 3. These micelles are constructed by the most probable configurations of the single-chain, representing the surfactants in equilibrium state. As we can see, in the first case, where the micelle consists of flexible surfactant chains is smaller than the micelle composed of rigid chains due to the fact that stiffness forcing the micellar core to be bigger, as the tails are unable to collapse. Finally, with respect to the micellar architecture, no deviations from the spherical symmetry were observed.



**Figure 5.** Schematic representation of aggregates, correspond to the minimum of standard chemical potential differences, for surfactants with 20 hydrophilic head units and 23 hydrophobic tail units and with different chain flexibility. A) Aggregate corresponds to a series of total flexible surfactant chains. B) Aggregate corresponds to a series of total rigid surfactant chains.

## Conclusions

In the present work, a series of simulations for a coarse-grained Pluronic model L44 (EO<sub>10</sub>PO<sub>23</sub>EO<sub>10</sub>) in water at a constant temperature of 37 °C, have been used in order to study the effect of changing the surfactant chain flexibility in the micellization behavior. SCMF theory was used as our tool for fast and good quality simulation results.

Critical Micelle Concentration (CMC), aggregation number and micellar size and architecture was investigated while progressive changes in surfactant chain flexibility occurred. Arbitrarily changes in the number of Kuhn segments allowed us to change the flexibility either of the entire chain or, selectively of the hydrophobic tails or the hydrophilic head.

The Critical Micelle Concentration (CMC) as well as the aggregation number were sensitive to this change. On increasing the chain stiffness, CMC becomes lower while the aggregation number is growing strongly.

This significant increase is due to easier and energetically more favorable packing of stiff chains. Furthermore, stiffening only the tails leads to larger aggregates than stiffening the head units. This is attitude to the fact that stiff tails are forcing the micellar core to be bigger, as the tails are unable to collapse.

In order to study better those results, we analyzed the density profiles of every flexibility case aggregate.

By observing the distribution function of the heads, tails and solvent molecules, we concluded that stiffer surfactant chains lead to larger micelles with much greater aggregation number than the flexible surfactant chains. This is attribute to the fact that, aggregates with stiffer surfactant chains, have higher tails concentration near the micellar core than aggregates composed of flexible chains. This means that the favorable interactions between the tails lead to a decrease in the free energy of the system. Finally, the schematic representation diagrams of aggregates composed of different surfactant chain flexibility, with respect to the micellar architecture, show that there are no deviations from the spherical symmetry.

To conclude, It will be very interesting for the future, to expand this work in order to study the same effect of changing the surfactant chain flexibility in the dynamic part of the micellization process.

## Acknowledgment

Financial support for this work has been provided by the University of Rovira i Virgili, through the master scholarship.

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