Molecular Simulations Study of the $C_{12}E_4$ Reverse Micelles changes with the Temperature and Pressure.

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Introduction

Poly(oxyethylene) glycols of the family C_iE_j can form a various mesophases depending the experimental conditions (such as concentration of the surfactant, the temperature, the hydrophile-lipophile balance etc…). In high concentration of non polar solvent (i.e. <75 % w/w), C_iE_j forms stable reverse micelle (RM). A key structural parameter is the ratio $W_o=[H_2O]/[Surf]$ which determines the micellar properties (such as size, entrapped water properties or polar group hydration.).

Experimental [1] and theoretical [2] studies indicate that the size, the shape and the hydration of surfactant (namely the number of water par EO unit) can be modulate with the temperature and the pressure and depend, in part, of surfactant conformation and the water core structure.
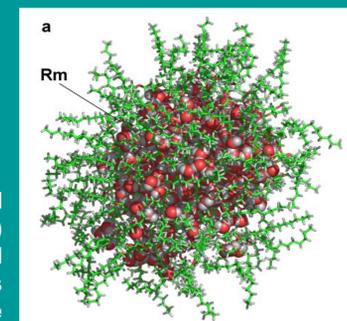
We present, here, a compared MD study of two types of RM in decane with the $C_{12}E_4$ Ethylene-Oxide heads (EOh) in different conformations (i.e. *all-trans* (RM94a) and in helix conformation (i.e. *gauche*: RM94b)).

We have evaluated by MD (10 ns each), the temperature and the pressure impact on the structure and hydration of the micelles depending the conformation of their surfactant headgroup. The RM were simulated at two temperatures (T=8°C and 25°C) and pressures (P=0.1 MPa and 200 MPa) with the ORAC MD package [3].

$C_{12}E_4$ [$(CH_3)-(CH2)_{10}-(CH_2-O-CH_2)_4-CH_2-OH$] is a class of non-ionic surfactant molecule whose the polar headgroup (EOh) can fold in α-helix in water [3]. The ratio between the hydrophilic and the hydrophobic regions is close to 1. Experimentally its aggregation number for $W_o=3$, is around 94 and the micellar structure was estimated to be spherical at 8° and become an ellipsoid at 25° [4].
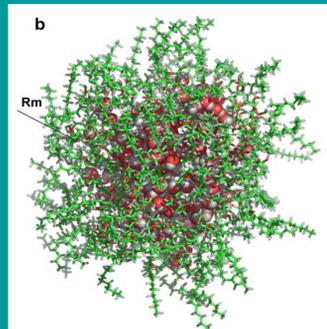
The pictures show the final configurations (T=10ns) of (RM94a (a)) and RM94b (b)) at T=25°C and P=0.1MPa. In RM94a, the water is trapped by the hydrophilic head of the surfactant, whereas in RM94b, the water forms a water cluster in the core of the micelle, surrounded by the EOh. This particular location of the water modify the reaction of the micelles with the temperature and the pressure.
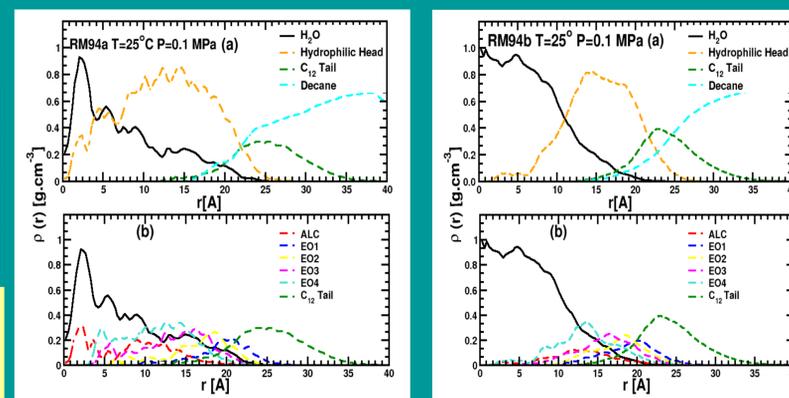

RM94a

T=25°C P=0.1MPa	a/c	ecc
Micelle (M)	1.24±0.01	0.56±0.01
Water Core (W)	1.33±0.08	0.64±0.06

RM94b

T=25°C P=0.1MPa	a/c	ecc
Simulated (M)	1.19±0.02	0.54±0.04
Water Core (W)	1.56±0.15	0.76±0.04

R_g (Å)	R_g^{hc}	R^M	A_s/Head (Å²)
Sim. (a)	17.73±0.32	21.65±0.17	42.05±1.53
Sim. (b)	17.54±0.31	20.05±0.07	41.12±0.37
Exp. [1]	19.93±1.00	25±1.0	52.94 ± 1.0

These tables present the averaged shape and size parameters for the micelles. The superscript M and hc give the radius of gyration of the entire micelles, the aqueous core respectively. The eccentricity indicates the extent deviation of the RM from an ideal sphere (i.e. ecc=0). a/c gives the average ratio between the major, a, and c, he minor semiaxes. The average surface per $C_{12}E_4$ was obtained with the expression: $As=4\pi(R_g^{hc})^2/94$ assuming a spherical shape for the micelles usually found in the literature.

On the figures, we present the averaged radial profiles for RM94a and RM94b. EO_{1-4} gives the EO position along the surfactant chain. ALC is the hydroxyl group of the head. As we can see, the water (black) in RM94a are mainly trapped in the hydrophilic region of the surfactant in contrast with RM94b. This will suggest a different response of this RM with the T and P.

RM94	(a) 8°C	(a) 25°C	(b) 8°C	(b) 25°C
	Δ^T		Δ^T	
$(a/c)^M$	+0.02 s		+0.02 s	
$(a/c)^W$	+0.08 s		+0.05 s	
$(R_g)^M$	+0.03 ns		+0.00 s	
$(R_g)^{pc}$	+0.06 s		-0.06 ns	
A_s/Head (Å²)	+1.47 s		+0.03 ns	
$Surf^M$ (Å²)	+1567 s		+464 s	

Structural changes of the micelles with the temperature. When T increase the two micelles become less spherical (especially for their water cores) with an increase of their polar cores. A significant augmentation of the surface in contact of the surfactant head with micellar water (As/Head) for RM94a. With the temperature the ASA contact with the oil (80% due of the C_{12} tail and water less than 1% and computed with Voronoï polyhedra also increase. Note s means significant, ns: no significant.

RM94	0.1MPa	200MPa	0.1MPa	200MPa
	Δ^P		Δ^P	
$(a/c)^M$	+0.02 s		+0.01 s	
$(a/c)^W$	-0.03 ns		+0.03 s	
$(R_g)^M$	-0.11 s		-0.10 s	
$(R_g)^{pc}$	-0.11 s		-0.15 s	
A_s/Head (Å²)	-0.49 s		-0.68 s	
$Surf^M$(Å²)	-599 s		-216 ns	

Structural changes of the micelles with the pressure. When the pressure increase, the micelles become more flattened and we observe a small reduction of their radii. The effect of the high pressure on the micelles is more marked for RM94b than for RM94a due again to their different structure. Note s means significant, ns: no significant.

Effect of the Temperature
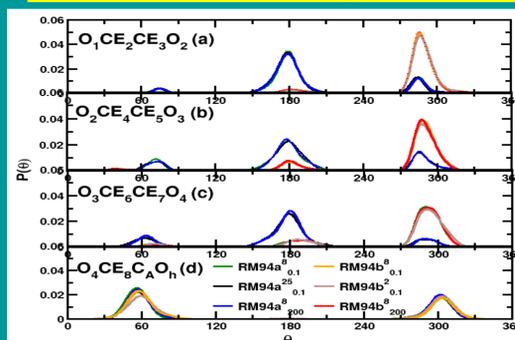
On the figure, we show the averaged normalized dihedral populations, $P(\phi)$, for the OCECEO angles of the $C_{12}E_4$ headgroup. $P(\phi)$ were not significantly modified with the T and P. We also observe that the number of transitions T->G for these angles increase with their proximity of the water core. For the angles far from the core the initial conformations remains. This discrepancy with others simulations can be explained by the low hydration of this region for this size of micelle. For the last torsion, we observe a *gauche*+- conformation (stabilized by water H-bonds) in agreement with others MDs of these class of surfactant in others phases (L_1 or L_α).

Impact of the Pressure

RM94	Vol (Å³)/Mol			
	0.1MPa	200MPa	ΔV	$K^{200}_{0.1}$ %
Total	606816.5	533314	73502.5	12.1
Decane	334	289.5	44.5	13.3
Micelle	71685.5	67059.5	4626.0	6.4
$C_{12}E_4$	671.5	622.0	49.5	7.4
C_{12}	361.5	324.5	37.0	10.2
EO_{1-4}	281.5	271.5	10.0	3.5
ALC	27.5	26.3	1.2	4.3
H_2O	30.3	28.4	1.9	6.2
Bulk H_2O	30.4	28.0	2.4	7.90

The average molecular volumes for the two micelles, the fluctuations and the corresponding compression ($K^{200}_{0.1} = (V_{0.1} -V_{200})/V_{0.1}$) for the solvent, micelles, surfactant regions and the micellar water reflect the different compressibility regions for the aggregate. A comparison with the pure SPC bulk water is made.

RM94	(a 8°C	(a) 25°C	(b) 8°C	(b) 25°C
	Δ^T_{hyd}		Δ^T_{hyd}	
O_1-O_w	-0.05 ns		-0.12 s	
O_2-O_w	-0.02 ns		-0.21 s	
O_3-O_w	-0.02 ns		-0.23 s	
O_4-O_w	-0.04 s		-0.20 s	
O_h-O_w	-0.07 s		-0.08 s	

The surfactant EOh hydration with the T computed with the pdf O_n-O_w. First, we have found that for each T the number of water in the first shell of the EO oxygen atom increase linearly as the function the distance to core: 0.4 to 1.4 for O_1 and respectively. We found that for RM94a occurs only for O_4 and O_h atoms. Whereas for RM94b, the dehydration is significant for all the EO units and the O_h group. With P (not shown), we observe, in opposite, an increase of the number of water per EO and the hydroxyl group (close to 10% and 25% respectively), related once again with their accessibility to the water core. Note s means significant, ns: no significant.

Conclusion

Our MD indicates that low water content small RM decreases significantly the response of aggregates and C12E4 to P and T-

- For the RM with the EOh in *gauche* conformation, the dehydration occurs for all the oxygen atoms, in contrast to the all-trans micelle.

- We observe a small number of transitions T->G of the Eph dihedral angles, related to their positions to the water core independently the increase of T and P.

- When P increases, we observe a small reduction of the RM and water core radii and the EOh hydration increases. The computation of the volumes of some micelles regions indicates that the micelles present different compartments with different compressibility/rigidity: C_{12}>ALC $\geq E_4$) and C_1E_4.> H_2O.

- Is our datas can be generalized for bigger RM? For response, we plan to use coarse grain model of surfactant or simulate in implicit solvent to increase the size of the system and reduce the computational cost.

Methodology Notes

- We used CHARMM and Tasaky force field [4] to model the $C_{12}E_4$, the decane, the water (SPC).

- The systems were setting up to be located in L_2 region of phase diagram of $C_{12}E_4$ /Water/decane (i.e. with an oil weight fraction (> 85%)) according [1] for a total of ~60000 atoms each.

- We used SPME for electrostatic (10 Å cutoff) with PBC [3].

- An 12 fs time step was used for the equation of motions with a r-RESPA [3]. The trajectories were saved every 240 fs for analysis for a simulation time of 10ns.

Bibliography

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