Structural properties of oil/water microemulsion with surface grafted PEO polymers

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Abstract: In this study, we investigated the structural properties of oil/water microemulsions with surface grafted polymers. In particular, we determined the effect of the addition of two kinds of hydrophobically modified polymers, PEO-m with one hydrophobic end and PEO-2m with two hydrophobic extremities. We used Molecular Dynamics simulations with the appropriate interaction potential that considers the VDW interactions, the electrostatic interactions, and the interaction induced by the polymers. Our results showed that the PEO-m introduces a steric repulsive interaction between the microemulsions in the diluted and concentrated systems, respectively, Φ=2.8% and Φ=14%. Thus, PEO-m favorises the stability and dispersion of the microemulsions. Besides, the PEO-2m introduces an attractive interaction between the droplets in the diluted case. Both PEO-2m and PEO-m strengthen the repulsive potential between the microemulsions in the concentrated case.

1. Introduction
Microemulsions are great candidates as potential drug delivery systems because they improve drug solubilization, long shelf-life, and ease of preparation and administration [1]. A microemulsion is defined as a thermodynamically stable liquid dispersion consisting of an aqueous and an oily phase combined with a surfactant [2,3]. It comes in the form of water droplets in oil or oil droplets in water, but these must be stabilized to prevent them from recombining because when two droplets come into contact, they combine naturally to minimize surface energy. To stabilize the emulsion droplets, amphiphilic molecules, such as surfactants, are often added, which reduce the interfacial tension in both phases. For drug delivery applications, nano-transporter are often covered with biocompatible polymers [4,5]. In this study, PEO is used in two different modified forms that we note, respectively, PEO-m and PEO-2m. The PEO-m refers to the PEO 227 plus C_{12}H_{25} alkane chain attached to one of its extremities. The latter permits graft of the PEO 227 to the microemulsions. The PEO-2m denote the PEO 227 plus two C_{12}H_{25} grafted to each one of its extremities.

In the Molecular Dynamics simulation (MD), microemulsions are considered to be non-overlapping, uniformly charged nanospheres interacting via an effective potential based on the DLVO model, which is
the sum of the repulsive potential of a hard-sphere, the van der Waals attractive term [6] and the Yukawa type screened Coulombic repulsive potential [7]. Besides, the presence of PEO-m with different quantities induces a steric-type repulsive interaction. The PEO-2m produces an additional attractive interaction potential related to the microemulsions bridging by the hydrophobic ends of the PEO-2m chains. The interaction potential parameters are already validated by the equation (OZ) method, with the approximation HNC [8].

In this work, we use molecular dynamics simulation to study the effect of the addition of the polymers PEO-m and PEO-2m on the structural and interaction properties of a spherical nanodroplet of positively charged O/W microemulsion. In this context, we use an ionic microemulsion comprising cetyl pyridinium chloride (CpCl) as a cationic surfactant, n-Octanol as co-surfactant, decane oil, and saltwater. We add a telechelic polymer PEO-m or PEO-2m to the microemulsion. This polymer consists of a water-soluble poly(ethylene oxide) (PEO), which has one or two hydrophobic ends (C_{12}H_{25}). PEO-m decorates the microemulsion nanodroplets, whereas PEO-2m has two possible configurations: bridging two different nanodroplets or decorating them.

![Figure 1. Schematic representation of two suspensions in the diluted and concentrated cases: Microemulsion droplets + polymer with one functional end (PEO-m); Microemulsion droplets + polymer with two functional ends (PEO-2m)](image)

2. Molecular Dynamics simulation (MD)

2.1 Interaction potential

Molecular dynamics consists of calculating the evolution of an interacting particle system over time. This simulation is used as structural and dynamic models for understanding the experimental results, provided that the potential for interaction between the particles, which make up the system, is known. In the case of a system consisting of ionic microemulsion, particles are modeled as uniformly charged hard spheres. The potential that models the interactions between each pair of microemulsions is the sum of a hard-sphere potential and a Van der Waals potential, and a Coulombic potential [9-10].

\[ U(r) = U_{HS} + U_{VDW} + U_{coulomb} \]
With $U_{HS}$: is the repulsive potential of a hard-sphere.

$$ U_{HS} = \begin{cases} +\infty, & r \leq 2R \\ 0, & r \geq 2R \end{cases} $$

$U_{VDW}$: is the attractive potential of Van der Waals

$$ U_{VDW} = \begin{cases} \frac{-A_H}{6} \frac{2R^2}{r^2} + \frac{2R^2}{r^2} + \ln\left(\frac{r^2 - 4R^2}{r^2}\right), & r \leq R_c \\ 0, & r > R_c \end{cases} $$

$U_{coulomb}$: A Yukawa-style coulombic repulsive potential:

$$ U_{coulomb} = \begin{cases} k_B T \frac{2}{1 + k R} \frac{e^{-k(r-R)}}{r}, & r \leq R_c \\ 0, & r > R_c \end{cases} $$

Where, $r$ is the distance from centre to centre, $A_H = 1.1 K_B T$ is the Hamaker constant, $R = 62\text{Å}$ is the radius of the microemulsions, $Z_{eff}$ is the effective charge per nanodroplet and $k$ is the Debye length, $l_B = \frac{e^2}{4\pi \varepsilon_0 \varepsilon_l K_B T}$ is the Bjerrum length, $\varepsilon_r = 80$ the dielectric constant of water and $\varepsilon_0$ with Permittivity of Vacuum, the temperature $T$ will be set to the value of the ambient temperature 298 $K$ and the effective charge per nanodroplet at $Z_{eff} = 130$, this value is taken from a previous structural study on this system revealed that an excellent quantitative agreement is found for all spectra with the same effective charge on each nanodroplet [11]. $R_c$ is a cut off distance, of the interaction potential.

When PEO-m is added to the bare microemulsion, we have seen an additional repulsive contribution linked to the decoration of the nanodroplets by the PEO-m chains:

$$ U_2 = U_{HS} + U_{VDW} + U_{coulomb} + V(r) $$

$V(r)$: A steric-type steric repulsive interaction of the Yukawa type:

$$ V(r) = \begin{cases} V_{steric} \left(\frac{2R}{r}\right) e^{-\frac{r-2R}{\lambda_{steric}}}, & r \leq R_c \\ 0, & r > R_c \end{cases} $$

$V_{steric}$ is the contact potential, $\lambda_{steric}$ is the range of interaction we assume of the order of magnitude of the PEO radius of gyration.

And when we add the PEO-2m with two ends on the bare microemulsion. In this case, we have seen an additional attractive contribution linked to the bridging of the nanodroplets by the PEO-2m chains:

$$ U_3 = U_{HS} + U_{VDW} + U_{coulomb} + V_{steric} + W_{bridging} $$

$W(r)$ Attractive Yukawa bridging type interaction:

$$ W(r) = \begin{cases} W_{bridging} \left(\frac{2R}{r}\right) e^{-\frac{r-2R}{\lambda_{pontage}}}, & r \leq R_c \\ 0, & r > R_c \end{cases} $$

$W_{bridging}$ the contact potential and $\lambda_{pontage}$ the range of the interaction, which should be of the order of magnitude of the average distance between the two ends of the PEO chain (~100 Å) [16].

Figure 2 illustrates the interaction potential, which is used in MD simulations, schematised using the parameters discussed above, with $(V_{steric} = 2.6 K_B T$ for Np=4(PEO-m), $V_{steric} = 5.2 K_B T$ for Np=8(PEO-
m)) and \( V_{\text{steric}} = 2.6K_B T \), \( W_{\text{bridging}} = -0.53K_B T \) for \( N_p=4(\text{PEO-2m}) \) and \( V_{\text{steric}} = 5.2K_B T \), \( W_{\text{bridging}} = -1.05K_B T \) for \( N_p=8(\text{PEO-2m}) \) and \( \sigma = 2R \).

\[ U(r) = K_B T \]

**Figure 2.** Dimensionless pair-potential between microemulsions, \( U(r) = K_B T \), versus the dimensionless distance \( r/\sigma \) (\( \sigma = 2R \)).

In this work, NVT MD simulations were performed, using the LAMMPS simulation package [17], in a cubic box of volume \( V \). We considered \( N = 10^6 \) microemulsions in the simulation box. We applied three-dimensional periodic boundary conditions to suppress the bord effect and simulate an infinite system [18].

3. Results and discussions

3.1 Static properties

Molecular dynamics is applied here to determine the structural properties of the bare microemulsion (\( N_p=0 \)), microemulsion with PEO-m polymer addition, and microemulsion with PEO-2m polymer addition.

**Figure 3.** Comparison of the pair correlation function \( g(r) \), for the bare microemulsion (\( N_p = 0 \)) and microemulsions with added PEO-m (\( N_p=4, N_p=8, N_p=12 \)), for two volume fractions (\( \Phi=2.8\% \) and \( \Phi=14\% \)).
We present in figure 3 the radial distribution function $g(r)$ for a mixed system of microemulsion and polymer PEO-$m$ in the diluted case $\Phi=2.8\%$ and the concentrated case $\Phi=14\%$. For $\Phi=2.8\%$, we observe a single correlation peak less intense and larger, which representing the interactions between the first close neighbors. We notice that when the parameter $N_p$ increases from 0 to 12(PEO-$m$), the correlation peak shifts towards greater distances, then the peak becomes less intense and larger. It varies from $(g_{\text{max}}=1.06074, d \sim 165.54\text{Å})$ to $(g_{\text{max}}=1.02415, d \sim 230.02\text{Å})$ see Table 1. For $\Phi=14\%$, we notice that the correlation function represents a more intense and narrower main peak representing the interactions between close neighbors and a second peak, less intense and wider, representing the interactions between second neighbors. The same remarks have been noticed when the parameter $N_p$ increases from 0 to 12(PEO-$m$), the correlation peak shifts towards greater distances, becomes more pronounced, and varies from $(g_{\text{max}}=1.44173, d \sim 159.96\text{Å})$ to $(g_{\text{max}}=1.52909, d \sim 189.72\text{Å})$. This result shows that the addition of PEO-$m$ to the microemulsion introduces a repulsive contribution to the existing interaction through a certain interpenetration resistance between the microemulsions in the diluted case and the concentrated case, as can be seen from Figure 4.

![Figure 4](image)

**Figure 4.** The mean field interaction potential $U_{\text{eff}}(r)=-k_B T \log(g(r))$ of microemulsions without PEO-$m$ ($N_p=0$) and with PEO-$m$ ($N_p=4, 8$ and 12) for $\Phi=2.8\%$ and $\Phi=14\%$.

**Table 1.** Analysis of the $g(r)$ curves obtained by MD for $N_p=0$(PEO-$m$), 4(PEO-$m$), 8(PEO-$m$) and 12(PEO-$m$) in the diluted case ($\Phi=2.8\%$) and the concentrated case ($\Phi=14\%$).

|          | $\Phi=2.8\%$ |          | $\Phi=14\%$ |
|----------|---------------|----------|--------------|
|          | $r_{\text{max}}$ | $g_{\text{max}}$ | $r_{\text{max}}$ | $g_{\text{max}}$ |
| $N_p=0$(PEO-$m$) | 165.54 Å  | 1.06074  | 159.96 Å  | 1.44173   |
| $N_p=4$(PEO-$m$) | 205.22 Å  | 1.03123  | 174.84 Å  | 1.35771   |
| $N_p=8$(PEO-$m$) | 222 Å     | 1.02132  | 182.28 Å  | 1.43607   |
| $N_p=12$(PEO-$m$) | 230.02 Å  | 1.02415  | 189.72 Å  | 1.52909   |
In this part, we will discuss the effect of the POE-2m on the correlation function $g(r)$ of the bare microemulsion for the diluted case $\Phi=2.8\%$ and the concentrated case $\Phi=14\%$. In figure 5, we present the correlation function of a microemulsion $N_p=0$ (POE-2m) and the correlation function of a microemulsion with polymer 4(POE-2m), 8(POE-2m), and 12(POE-2m) in the diluted case $\Phi=2.8\%$ and the concentrated case $\Phi=14\%$. For $\Phi=2.8\%$, we notice that the correlation peak shifts to smaller distances and becomes more intense and narrower as the $N_p$ parameter increases from 0(POE-2m) to 12(POE-2m) (see Table 2), which means the appearance of an attractive effective interaction between the microemulsions introduced by the POE-2m, as can be seen from Figure 6 (left). But for the concentrated case $\Phi=14\%$, the first peak becomes pronounced with the addition of the POE-2m, and it moves to large distances (varies from 159.96 Å to 186.55 Å) when the $N_p$ parameter increases from $0$(POE-2m) to 8(POE-2m). This shows that the addition of the POE-2m to the bare microemulsion in the concentrated case introduces a repulsive contribution between the microemulsions, as can be observed in Figure 6 (right).

Table 2. Analysis of the $g(r)$ curves obtained by MD for $N_p=0$ (POE-2m), 4(POE-2m), 8(POE-2m) and 12(POE-2m) in the diluted case ($\Phi=2.8\%$) and the concentrated case ($\Phi=14\%$).

| $\Phi$ | $r_{\text{max}}$ | $g_{\text{max}}$ | $r_{\text{max}}$ | $g_{\text{max}}$ |
|-------|-------------------|-------------------|-------------------|-------------------|
| $2.8\%$ | 165.54 Å | 1.06074 | 159.96 Å | 1.44173 |
| $4(\text{POE-2m})$ | 161.82 Å | 1.6182 | 174.84 Å | 1.36769 |
| $8(\text{POE-2m})$ | 158.1 Å | 1.69437 | 182.28 Å | 1.426 |
| $12(\text{POE-2m})$ | 154.53 Å | 1.91 | 186.55 Å | 1.515 |

These results showed that the addition of a PEO-m polymer on a bare microemulsion introduces a steric repulsive interaction between the nanodroplets, in the case of a concentrated system $\Phi=14\%$ and a diluted system $\Phi=2.8\%$. This interaction is repulsive at a distance shorter than the polymer size due to the confinement resistance, and the addition of a polymer-modified at two ends PEO-2m on a microemulsion introduces an attractive interaction between the droplets in the diluted case ($\Phi=2.8\%$). On the other hand, the PEO-2m and PEO-m strengthen the repulsive potential between the microemulsions in the concentrated case ($\Phi=14\%$).
Conclusion

In this work, we used molecular dynamics simulation to study the structure of oil/water microemulsions with associative polymers (PEO-m and PEO-2m). We were able to compare the effect of the following two polymers: PEO-m and PEO-2m, on the radial distribution function and the mean effective interaction. We notice the addition of PEO-m with different amounts on the bare microemulsion introduces repulsive interactions between the droplets for all volume fractions. On the other hand, the PEO-2m addition to the bare microemulsion introduces an attractive bridging interaction between the droplets in the diluted case. In contrast, it acquaints a repulsive interaction between the droplets in the concentrated case. Then the additions of the polymers POE-2m and POE-m have the same effect on the microemulsion in the concentrated microemulsions systems.
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