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Aggregate-based sub-CMC Solubilization of Hexadecane by Surfactants

Hua Zhong[1,2,3*], Lei Yang[1,2], Guangming Zeng[1,2], Mark L. Brusseau[3], Yake Wang[3], Yang Li[4], Zhifeng Liu[1,2], Xingzhong Yuan[1,2], Fei Tan[1,2]

[1] College of Environmental Science and Engineering, Hunan University, Changsha 410082, China;

[2] Key Laboratory of Environmental Biology and Pollution Control (Hunan University), Ministry of Education, Changsha, 410082, China;

[3] Department of Soil, Water and Environmental Science, University of Arizona, Tucson, Arizona 85721, U.S.A;

[4] Department of Chemistry, University of Science and Technology of China, Hefei, 230026, China.

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Email Addresses:

Hua Zhong: zhonghua@email.arizona.edu

Lei Yang: wlwyanglei@126.com

Guangming Zeng: zgming@hnu.edu.cn

Mark L Brusseau: brusseau@email.arizona.edu

Yake Wang: yakew@email.arizona.edu

Yang Li: ly2013fi@mail.ustc.edu.cn

Zhifeng Liu: lzf18182002@163.com

Xingzhong Yuan: yxz@hnu.edu.cn

Fei Tan: tanfei_2013@163.com

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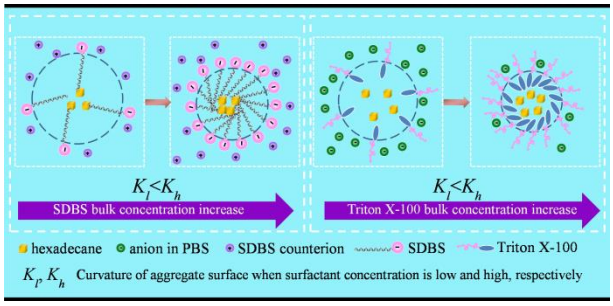

SDBS or Triton X-100 at sub-CMC concentrations enhances hexadecane solubilization due to aggregate formation mechanism. The sub-CMC aggregate size decreases with increasing surface excess of surfactant.

Abstract

Solubilizaiton of hexadecane by two surfactants, SDBS and Triton X-100, at concentrations near the critical micelle concentration (CMC) and the related aggregation behavior was investigated in this study. Solubilization was observed at surfactant concentrations lower than CMC, and the apparent solubility of hexadecane increased linearly with surfactant concentration for both surfactants. The capacity of SDBS to solubilize hexadecane is stronger at concentrations below CMC than above CMC. In contrast, Triton X-100 shows no difference. The results of dynamic light scattering (DLS) and cryogenic TEM analysis show aggregate formation at surfactant concentrations lower than CMC. DLS-based size of the aggregates (d) decreases with increasing surfactant concentration. Zeta potential of the SDBS aggregates decreases with increasing SDBS concentration, whereas it increases for Triton X-100. The surface excess (Γ) of SDBS calculated based on hexadecane solubility and aggregate size data increases rapidly with increasing bulk concentration, and then asymptotically approaches the maximum surface excess (Γ_{max}). Conversely, there is only a minor increase in Γ for Triton X-100. Comparison of Γ and d indicates that excess of surfactant molecules at aggregate surface has great impact on surface curvature. The results of this study demonstrate formation of aggregates at surfactant concentrations below CMC for hexadecane solubilization, and indicate the potential of employing low-concentration strategy for surfactant application such as remediation of HOC contaminated sites.

Keywords: surfactant, SDBS, Triton X-100, critical micelle concentration, solubilization, aggregation.

1. Introduction

Today surfactants have been a chemical that is ubiquitously used in industries and households. One well-known function of surfactants is to solubilize hydrophobic organic compounds (HOCs), which has been widely made use of, ranging from oily dirt removal from textiles for housekeeping to enhanced remediation of soil or aquifer contaminated by HOCs.[1-3] Solubilization enhancement of HOCs by surfactants has been the subject of many experimental and theoretical studies, especially at concentrations above CMCs.[4-10] Critical micelle concentration (CMC) is generally considered to be the concentration at which surfactant molecules aggregate to form micelles. Micelles are considered to be of spherical shape, and the size, shape, aggregation number, and stability of micelles vary according to temperature, surfactant concentration, and solution chemistry.[11] It is typically assumed that surfactants solubilize low-solubility compounds only at concentrations higher than CMC, through partitioning into the hydrophobic core of micelles.[9, 12, 13]

The results of some studies have shown, however, that solubilization enhancement may also occur at surfactant concentration below the CMC. Zhang and Miller[6] investigated solubilization of octadecane by rhamnolipid biosurfactant. Solubilization of octadecane was enhanced by rhamnolipid at concentrations below CMC, and the enhancement was much more significant than above CMC. Similar results were observed for hexadecane solubilization in the presence of a monorhamnolipid in our prior study.[14] Kile and Chlou investigated solubilization of

DDT by surfactant Triton and Brij, and enhancement of apparent DDT solubility was also observed below the nominal CMC.[5] To our knowledge, the mechanisms for these sub-CMC solubilization behaviors, for example the potential for aggregate formation below CMC, have not been systematically investigated in prior studies. Moreover, concerns about the ecotoxicology of surfactants, e.g. alkylphenol ethoxylates (APEs)[15, 16], has caused the implementation of strict emission controls for APEs in various industrial and consumer applications.[17-20] Thus, the ability for surfactants to achieve solubilization enhancement of HOCs at sub-CMC concentrations is of importance for cost and ecotoxicology considerations.

In this study, solubilization of *n*-hexadecane in the presence of SDBS or Triton X-100 surfactant was investigated, with a special focus on such behavior at surfactant concentrations below CMC. SDBS and Trion X-100 were selected to represent anionic and nonionic surfactant, respectively. In addition to hexadecane solubility, characterizations of the potential aggregation of the surfactants, such as aggregate particle size and zeta potential measurements and cryo-TEM-based aggregate observation, were implemented. Finally, based on surfactant interface adsorption theory, spherical aggregate assumption and surfactant mass balance, the aggregation formation and surfactant partitioning mechanism was raised to interpret the sub-CMC hydrocarbon solubilization.

2. Theoretical

At a given temperature, adsorption of surfactant to the hexadecane/aqueous solution interface is related to interfacial tension and surfactant bulk activity as expressed by the Gibbs adsorption equation.[21] In this study, the adsorption of ionic and nonionic surfactant at the interface in the presence of swamping counterion (electrolyte solution) can be described by equation (1):

$$\Gamma = -\frac{a}{RT}\left(\frac{\mathrm{d}\gamma}{\mathrm{d}a}\right) \times 10^{-3} \quad (1)$$

where a is the surfactant bulk activity (mol/L); R is the universal gas constant (8.314 J/(mol·K)), T (K) is the absolute temperature; Γ (mol/m^2) is the interface excess of the surfactant; γ (mN/m) is the interfacial tension.

Surfactant adsorption at fluid-fluid interfaces is described by the Langmuir equation at concentrations below the critical micelle concentration (CMC)[8, 22]:

$$\Gamma = \Gamma_{\max}\frac{Ka}{1+Ka} \quad (2)$$

where $\Gamma_{\max}$ (mol/m^2) is the maximum interface excess of surfactant and K (L/mol) is the Langmuir constant.

Resolving equation (1) and combining it with equation (2) give the Szyszkowski equation, which describes interfacial tension as a function of surfactant bulk activity at concentrations below CMC:

$$\gamma_0 - \gamma = RT\Gamma_{\max}\ln(1 + Ka) \times 10^3 \quad (3)$$

where γ_0 (mN/m) is the interfacial tension of the solution in the absence of surfactant. The relation between a and the freely-dissolved surfactant monomer concentration, C_w (mol/L), is:

$$a = fC_w \quad (4)$$

where f is the activity coefficient of surfactant. The concentration of surfactants in bulk solution is relatively low (<0.01 mol/L) in this study, thus f is very close to 1 and $a \approx C_w$.[22]

Based on the classical model regarding the structure of alkane-surfactant aggregates formed in solution for alkane solubilization, the aggregates are assumed to be spherical with a layer of surfactant molecules on the surface. Thus, when solubilization reaches equilibrium, equation (5) and (6) can be obtained based on mass balance of surfactant:

$$\frac{\Gamma A_{\mathrm{i}} C_{\mathrm{hex}} M_{\mathrm{hex}}}{\rho_{\mathrm{hex}}} \times 10^{-3} + C_{\mathrm{w}} = C_0 \quad (5)$$

$$A_{\mathrm{i}} = \frac{6}{d} \times 10^{-9} \quad (6)$$

where A_i (m^2/m^3) is the hexadecane-water specific interfacial area; C_0 (mol/L) is the total concentration of surfactant initially added; C_{hex} (mol/L) is the concentration of hexadecane solubilized in aqueous phase; M_{hex} (g/mol) is molecular weight of the hexadecane; and ρ_{hex} (g/cm^3) is the density of the hexadecane at given temperature T (K); d (nm) is the measured diameter of the aggregates. From equation (3), (4), (5) and (6), the surfactant excess, Γ, of surfactant on the aggregate surface and the C_w for a given C_0 can be obtained. The area per surfactant molecule at the hexadecane-aqueous interface (namely the aggregate surface), A (m^2), is obtained by equation (7):

$$A = \frac{1}{\Gamma N_{\mathrm{A}}} \quad (7)$$

where N_A (6.022×10^{23} mol^{-1}) is the Avogadro constant.

3. Materials and methods

3.1 Materials

SDBS (Sodium dodecylbenzenesulfonate, technical grade, purity > 97.0%), Triton X-100 (polyoxyethylene (10) isooctylphenyl ether, laboratory grade, purity > 98.0%), and hexadecane (purity > 99.0%) were purchased from Sigma-Aldrich (St. Louis, Mo., U.S.). Selected properties and molecular structures of SDBS and Triton X-100 are presented in Table 1 and Fig. 1, respectively. *n*-Octane (purity > 95.0%) and HPLC grade ethanol were purchased from Damao Chemical (Tianjin, China). All other chemicals were of analytical grade and used as received. Ultra-pure water with an initial resistivity of 18.2 MΩ·cm produced by UPT-Ⅱ-40 (Ulupure, Chengdu, China) was used throughout the experiment. Phosphate buffer solution (PBS, 1.24 g/L KH_2PO_4 and 1.35 g/L K_2HPO_4 $3H_2O$, pH 6.8) was used as the background electrolyte solution to provide a stable concentration of counterions, which is important for application of the Gibbs adsorption equation for surfactant surface excess calculation.

3.2 Interfacial tension measurement

In order to obtain the CMCs of the surfactants and Γ_{max} and K in equation (3), interfacial tension between hexadecane and surfactant solution with designated

surfactant concentrations was measured at 30 ℃ with a tensiometer (JZ-200A, Chengde, China) using the Du Noüy Ring method.[23] In brief, 15 mL of surfactant PBS solution was prepared in a 50 mL glass beaker. 15 mL of hexadecane was then carefully added to the top of the surfactant solutions without disturbing the bulk volumes. Before the interfacial tension was measured, the beaker was kept at 30 ℃ for half an hour to allow partition of surfactant to water-hexadecane interface to reach equilibrium. The measurements were reproducible, with the difference of duplicate measurements within ±0.2 mN/m.

3.3 Solubilization of hexadecane by surfactants

Solutions of SDBS and Triton X-100 with hexadecane were prepared in triplicates using the following procedures. 50 μL of hexadecane was pipetted to a 25-mL glass flask, and the flask was rotated to spread the hexadecane on the bottom of the flask. 10 mL of PBS solution of SDBS or Triton X-100 was then added to the flask and incubated on a reciprocal shaker at 30 ℃, 120 rpm for 72 h to allow the solubilization to reach equilibrium (result of a preliminary test showed that hexadecane solubility does not change after 72 h). Then the flasks were held stationary for 2 h to allow establishment of stable phase distributions. 4 ml of the aqueous solution was separated and collected using the method described by Zhong et al.[14]. 1 mL of the collected samples was removed for hexadecane concentration measurement, and another 2 mL was used for measurement on size and zeta

potential of the aggregate particles. The hexadecane concentration was measured using gas chromatography (Agilent GC 6890N) following the procedures described by Zhong et al.[14]. Samples with 8000 μM SDBS or with 1000 μM Triton X-100 were centrifugally filtered using 30KD ultrafiltration membrane (Millipore, Darmstadt, Germany) followed by hexadecane concentration measurement in the filtrate to check the partition of hexadecane. A control containing 10 mL surfactant solution and no hexadecane was used to quantify loss of surfactant due to adsorption to inner wall of the flasks. To examine the stability of solubilized hexadecane, 4 mL of the solubilized hexadecane solution obtained with 50 μM SDBS or 25 μM Triton X-100 were sealed and allowed to stand still for 48 hours. Then 3 mL of the solution were again centrifugally separated using the method described by Zhong et al.[14] and hexadecane concentration was measured.

The size and zeta potential of aggregate particles were measured using a ZEN3600 Zetasizer Nano (Malvern Instruments, U.K.). The particle size was determined through dynamic light scattering (DLS) at 633 nm with He-Ne laser, which worked on 4.0 mV power. 1 mL of sample was loaded to the DTS-0012 cell and kept at 30 ℃. The scattered light was collected by receptor at angle of 173 ° from light path. The size of the aggregates was expressed in terms of hydrodynamic diameter, which was calculated by using the software associated with the instrument. To obtain the zeta potential of the aggregates, approximately 1 mL of sample was loaded to the DTS1060 folded capillary cell and the electrophoretic mobility of the

aggregate particles was measured at 30 ℃ under automatic voltage using laser Doppler velocimetry with M3-PALS technique to avoid electrossmosis. The measured data was converted into corresponding zeta potential applying the Helmholtz-Smoluchowski equation.[24]

3.4 Cryo-Transmission Electron Microscopy (cryo-TEM) observation of aggregates

A 4 μL drop of sample was placed on the copper grid, and then sent to a FEI Vitrobot sample plunger. The excess sample was removed with filter paper. The grid was then immediately plunged into a bath of liquid ethane and transferred to a bath of liquid nitrogen. The samples were stored in a GATAN model cryo-transfer unit in liquid nitrogen. The morphology of surfactant-hexadecane aggregates was viewed with a Tecnai F20 cryo-transmission electron microscope (FEI, Hillsboro, Oregon) at 120 kV.

4. Results and discussion

4.1 Γ_{max} and K

The dependence of interfacial tension on the surfactant concentration is presented in Fig. 2a. The interfacial tension of hexadecane/PBS solution in the absence of surfactants is 41.3 mN/m. For SDBS, hexadecane/PBS interfacial tension decreases rapidly from 41.2 to 2.3 mN/m with increase of the SDBS concentration

192 to approximately 600 μM. Further increase in SDBS concentration has minimal
193 effect on the interfacial tension. For Triton X-100, the interfacial tension decreases
194 from 41.3 to 4.2 mN/m with increase in the Triton X-100 concentration to
195 approximately 500 μM. Further increase in Triton X-100 concentration slowly
196 reduces the interfacial tension from 4.2 to 1.4 mN/m.

197 CMCs of the surfactants were obtained using the method described by Zhong et
198 al.[25]. The CMC of SDBS is 612 μM, which is lower than in pure water (e.g. 2764
199 μM reported by Yang et al.[26]) due to the presence of counterions (i.e., K^+) in PBS in
200 this study. The CMC of Triton X-100 is 672 μM, which is in the range of 200-900
201 μM reported by Sigma-Aldrich.[27] The significantly different CMCs for PBS versus
202 water obtained for SDBS compared to the similar values obtained for Triton is
203 consistent with the anionic and nonionic natures of the two, respectively.

204 The interfacial tension data at surfactant concentrations below CMC were well
205 fitted by the logarithmic function described by Equation (3) (Fig. 2b), and the
206 maximum interface excess of surfactant (Γ_{max}) and the Langmuir constant (K) were
207 thus obtained. Minimal surfactant molecule area at interface (A_m) was calculated
208 using equation (7). The results are summarized in Table 1.

209

210 **4.2 Solubilization of hexadecane by surfactants**

211 As shown in Table S1, concentration of hexadecane solubilized by 50 μM
212 SDBS or 25 μM Triton X-100 after standing for 48 hours is essentially identical to

the initial concentration. 50 μM and 25 μM are lower end concentrations, respectively, for SDBS and Triton X-100 used in this study. The results demonstrate good stability of the solubilized hexadecane. Results of hexadecane solubilization by SDBS and Triton X-100 are presented in Fig. 3. Both surfactants increase the solubility of hexadecane at surfactant concentrations lower than CMC. The apparent solubility of hexadecane increased linearly with surfactant concentration for both surfactants, with different slopes below and above CMC. Solubilization capacity of a surfactant for an HOC is characterized by the molar solubilization ratio (MSR), which is defined as increase of solubilized hydrophobic compound concentration (mol/L) per unit increase of surfactant concentration (mol/L) in the solution.[12, 28] As shown from Fig. 3a, the MSR for SDBS is significantly higher below CMC than above CMC (i.e. 0.84 and 0.16, respectively). Similar results were observed for an ionic rhamnolipid biosurfactant in the solubilization of hexadecane[14] and octadecane[6]. In contrast, MSRs for Triton X-100 are not significantly different below and above CMC (1.9 and 1.5, Fig. 3b), indicating the influence of surfactant molecule structure on solubilization behavior.

4.3 Size and zeta potential of aggregates

Formation of aggregates at surfactant concentrations both below and above CMC is demonstrated by the results of aggregate size measurement using DLS method (Fig.4) and by direct view of the aggregates with cryo-TEM for Triton

X-100 at concentrations of 25 and 1500 μM (Fig. S1, Supplementary Information). Also, the spherical aggregate assumption was confirmed by the sphere morphology of the aggregates. Although three groups of particles with different size range (three peaks in the intensity and volume of particles distributions (%) plots, Fig. S2) were detected by DLS particle size measurement, almost 100% of the particles in numbers are in the group of the smallest size (Figs. S2 and S3). This is consistent with the results of the cryo-TEM measurements, in which only one group of particles with similar size was observed (Fig. S1). For both surfactants, the particle size decreases rapidly with increase of C_0 to approximately 200 μM, and then stabilizes as C_0 continues to increase to above CMC (Fig.4).

As shown in Fig. 5, for anionic surfactant SDBS, the zeta potential of aggregates decreases approximately from -20 mV to -35 mV with increase of C_0 from 25 μM to 200 μM, and stabilizes at ~ -35 mV with further increasing C_0 to 800 μM. Similar trend was observed by Ivanov et al.[29] for zeta potential of hexadecane emulsion drops versus concentration of ionic surfactant SDS at significantly low SDS concentrations. When C_0 is even further increased to 1200 μM, a secondary decrease of zeta potential to ~-70 mV is observed. In contrast, the zeta potential of hexadecane-Triton X-100 aggregates increased from -20 mV to -5 mV with increasing C_0 from 50 μM to 1000 μM and stabilized at ~-5 mV when C_0 was above 1000 μM. Zeta potential is the potential difference between the bulk solution of the dispersion medium and the slippery layer of fluid attached to the dispersed

particle.[24, 30] Due to the anionic hydrophilic heads of SDBS, the aggregates have negatively charged surface.[31] The negatively charged surface of aggregates for non-ionic Triton X-100 probably results from association of anions in PBS (i.e. OH^-, HPO_4^{2-}, $H_2PO_4^-$, PO_4^{3-}) with the polyoxyethylene chain of Triton on the aggregate surface.

4.4 Partitioning of surfactants and its relation with aggregation

In the experiments no emulsion of hexadecane in the presence of surfactants was observed. Adsorption of the surfactants to the inner wall of the flask was also minimal (data not shown). Because very limited volume of hexadecane (50 μL) was used, partition of surfactants to the hexadecane phase, or to the interface between the floating mass of hexadecane and the aqueous phase (less than 1 cm^2 in contrast to the magnitude of 10^2~10^4 cm^2 for the total surface area of the aggregates according to calculation below), was minimal. Therefore, the surfactants reside either in bulk aqueous solution or in the aggregate. The hexadecane concentration in the filtrate after ultrafiltration was under the detection limit (data not shown), showing that the amount of freely-dissolved hexadecane in bulk aqueous phase is minimal and all the solubilized hexadecane is associated with aggregate. This is consistent with the fact that hexadecane has extremely low water solubility (0.09 μg/L, 25 ℃) and high octanol-water partition coefficient ($10^{8.3}$, 25 ℃) of hexadecane.[32] Hence, based on the spherical aggregate assumption, the aggregate surface excess Γ and the bulk

concentration C_w of surfactants were calculated by applying equation (2) and (5) using Γ_{max} and K previously obtained.

For both SDBS and Triton X-100, a linear relationship between the apparent solubility of hexadecane, C_{hex}, and the freely-dissolved surfactant monomer concentration, C_w, is observed with increase of C_w to CMC (Fig. 6a). This is similar to the relationship between C_{hex} and the total surfactant concentration, C_0 (Fig. 3). By comparing the slopes of C_{hex}-C_0 profile at C_0 below CMC and C_{hex}-C_w profile (0.84 versus 1.0 for SDBS, and 1.9 versus 2.5 for Triton X-100), the relative distribution of the surfactant between the freely-dissolved and aggregate-associated is calculated. The percentage of the aggregate-associated surfactant is approximately 16% and 23% of the total for SDBS and Triton X-100, respectively.

Changes of surfactant surface excess (Γ) and molecule area (A) versus C_w are presented in Fig. 6b. For SDBS, a rapid increase of Γ and decrease of A are observed when C_w increases from ~25 μM to ~150 μM. Further increase of C_w causes asymptotic approach of Γ and A to Γ_{max} and A_m, respectively. Conversely, there is only a minor increase in Γ for Triton X-100. Only very slight increase of Γ and decrease of of A are observed when C_w was below ~80 μM. Γ and A are more sensitive to change of C_w with a smaller K according to equation (2) and (7). The K value for Triton X-100 is much larger than for SDBS (4.33×10^3 and 0.2×10^3 m^3/mol, respectively (Table 1)). Thus, a more significant change of Γ and A over a broader range of C_w occurred for SDBS.

As shown in Fig. 7, for both surfactants, aggregate size, *d*, decreases with the increase of surfactant surface excess on the aggregates, Γ, in a way that *d* approaches the stabilized minimum aggregate size (d_{min}) as Γ approaches Γ_{max}. This result indicates that the curvature of the aggregate surface increases with increasing surface density of surfactant molecules. For SDBS, which has charged hydrophilic head, as SDBS molecules approach each other (Γ increases and *A* decreases) on the aggregate surface, the electrostatic repulsion between charged heads of SDBS becomes stronger. Such enhancement in electrostatic repulsion induces unequal rate of approach for polar and hydrophobic moieties between molecules, and therefore increase in aggregate surface curvature (Fig. 8). Thus, the aggregate size, *d*, decreases with increasing Γ. Similarly, as the polar head of Triton X-100 molecule, the polyoxyethylene chain, usually twists and curls, causing large actual molecule radius[33], the spatial steric repulsion between Triton X-100 polar heads may act in a way similar to electrostatic repulsion between charged heads in SDBS molecules, thus also causing an increase in surface curvature of aggregates (Fig. 8).

Zeta potential is a function of particle size and surface charge density.[24, 34, 35] Because SDBS is an anionic surfactant with a polar head that fully dissociates in solution, surface charge density is determined by surface molecule density, or Γ. Also, as discussed above, particle size is also a function of Γ. For SDBS, therefore, zeta potential is essentially a dependent of Γ and its change also exhibits an asymptotic pattern at concentrations lower than CMC. For Triton X-100, binding of

318 anions, i.e. $H_2PO_4^-$, HPO_4^{2-} and OH^-, to the polyoxyethylene group through
319 hydrogen bond may be responsible for the negative zeta potential of the aggregates.
320 As Γ increases, the Triton X-100 molecules become more compacted on the
321 aggregate surface, leaving less space for the anions to partition. Consequently zeta
322 potential increases.

323 For the standard surfactant solubilization conceptualization, enhancement of
324 HOC solubility requires surfactant concentrations higher than CMC.[28, 36-38] In
325 contrast, results in this study show that significant hexadecane solubility
326 enhancement takes place at surfactant concentrations lower than CMC and such
327 enhancement is related to formation of aggregates. In fact, the CMC measurement
328 using the general methods, e.g. the interfacial tension and conductometric methods,
329 is based on a pure-surfactant micelle formation mechanism. We speculate that the
330 presence of hexadecane has some influence on surfactant monomers activity through
331 the hydrophobic interaction between surfactant and hexadecane molecules, which
332 may be more significant than between surfactant molecules themselves. Thus, the
333 interaction between surfactant and hexadecane molecules may favor formation of
334 aggregates in priority to formation of pure-surfactant micelles, leading to
335 hexadecane solubilization enhancement below CMC.

336 When surfactant concentration in the aqueous phase is higher than CMC, the
337 surfactant molecules form micelles. Co-existence of hexadecane-SDBS aggregates
338 and SDBS micelles is observed with Cryo-TEM at high magnification (Fig. S4). The

339 decreases in MSR and aggregate zeta potential for SDBS as C_w goes above CMC are
340 probably a result of micelle formation. At surfactant concentrations higher than
341 CMC, a new partitioning equilibrium of surfactant between the bulk solution,
342 hexadecane/water interface, and micelles is established. In this case, C_w remains at
343 CMC and is insensitive to the change of C_0, and so are Γ and d. Hence, the regime of
344 HOCs solubilizaiton by surfactants at concentrations above CMC differs from that
345 below CMC.
346

347 ## 5. Conclusion

348 In contrast to the conceptualized micelle-based mechanism for solubilization of
349 HOCs starting at surfactant concentration higher than CMC, the results of this study
350 demonstrated that SDBS and Triton X-100 at sub-CMC concentrations can enhance
351 hexadecane solubilization employing an aggregate formation mechanism.
352 Observation of sub-CMC aggregates by both DLS and cryo-TEM methods suggests
353 that HOC-surfactant interaction contributes to sub-CMC aggregate formation, which
354 is in contrast to pure-surfactant micelles formation above CMC. This is for the first
355 time the sub-CMC solubilization of HOCs by surfactants is comprehensively
356 explored. The study is of importance for better understanding the solubilization
357 behavior of HOCs by surfactants and for economical application of surfactants.
358 Future studies should aim at testing such sub-CMC solubilizaiton behavior for a
359 variety of surfactants and HOCs.

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Table 1 Selected properties and the water-hexadecane interface coefficients of the surfactants used in this study

Surfactant	*Formula*	*Surfactant type*	*Molecular weight* (g/mol)	*CMC*[a] (μM)	Γ_{max}[b] (mol/m^2)	A_m[c] (nm^2)	K[d] (m^3/mol)
SDBS	$C_{12}H_{25}C_6H_4SO_3Na$	Anionic	348.48	612	3.3×10^{-6}	0.50	0.2×10^{3}
Triton X-100	$C_8H_{17}C_6H_4O(CH_2CH_2O)_{10}H$	Non-ionic	648.86	672	1.9×10^{-6}	0.87	4.3×10^{3}

[a] Critical micelle concentration (CMC) measured in PBS solution at 30 ℃

[b] Maximum interface excess of surfactant

[c] Area per surfactant molecule at $\Gamma_{max.}$

[d] Langmuir equation constant

Figure 1 The molecular structure of SDBS and Triton X-100.

Figure 2 (a) The hexadecane/PBS interfacial tension as a function of surfactant concentration. (b) Interfacial tension-concentration relation regression at surfactant concentrations below CMCs using Szyszkowski equation (Equation (3) in text).

Figure 3 Apparent hexadecane solubility (C_{hex}) versus total surfactant concentration (C_0) of (a) SDBS and (b) Triton X-100. Two sets of regression represent data for below and above the CMCs.

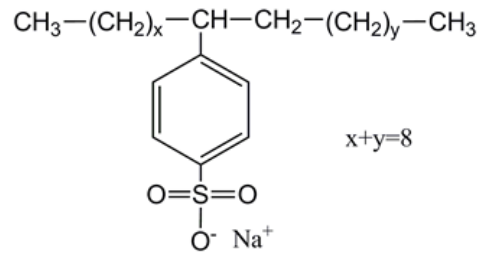
Figure 4 Aggregate size (d) versus the total surfactant concentration (C_0) for hexadecane solubilization. (Insert) Zoom-in for C_0 lower than CMC.

Figure 5 Zeta potential of aggregates versus the total surfactant concentration (C_0) for the hexadecane solubilization.

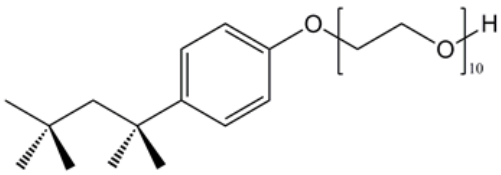
Figure 6 (a) Apparent solubility of hexadecane (C_{hex}) versus the bulk surfactant concentration (C_w) at C_w below CMCs; (b) surface excess (Γ) and molecule area (A) of surfactants on the aggregates surface versus surfactant bulk concentration (C_w). The dash lines and dash dot lines represent the maximum surface excess (Γ_{max}) and the minimum area per surfactant molecular on the surface (A_m), respectively.

Figure 7 Aggregates diameter (d) and surface excess of surfactants (Γ) versus the bulk surfactant concentration (C_w) blow CMCs.

Figure 8 Schematic diagram of aggregate formation at surfactant concentration below CMCs and the change of curvature of aggregates surface with increasing surfactant bulk concentration for the hexadecane solubilization by surfactant.



SDBS



Triton X-100

Figure 1

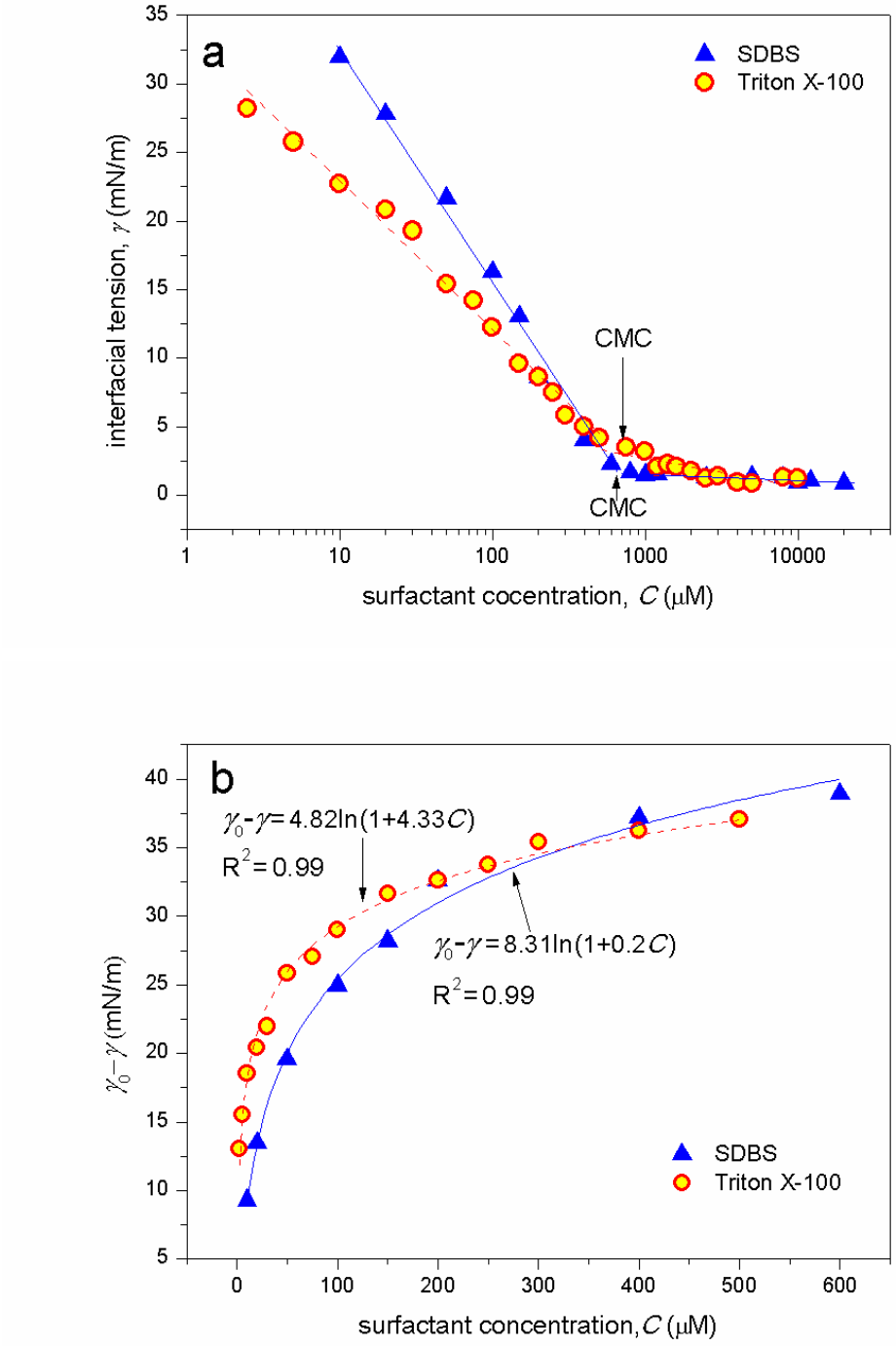


Figure 2

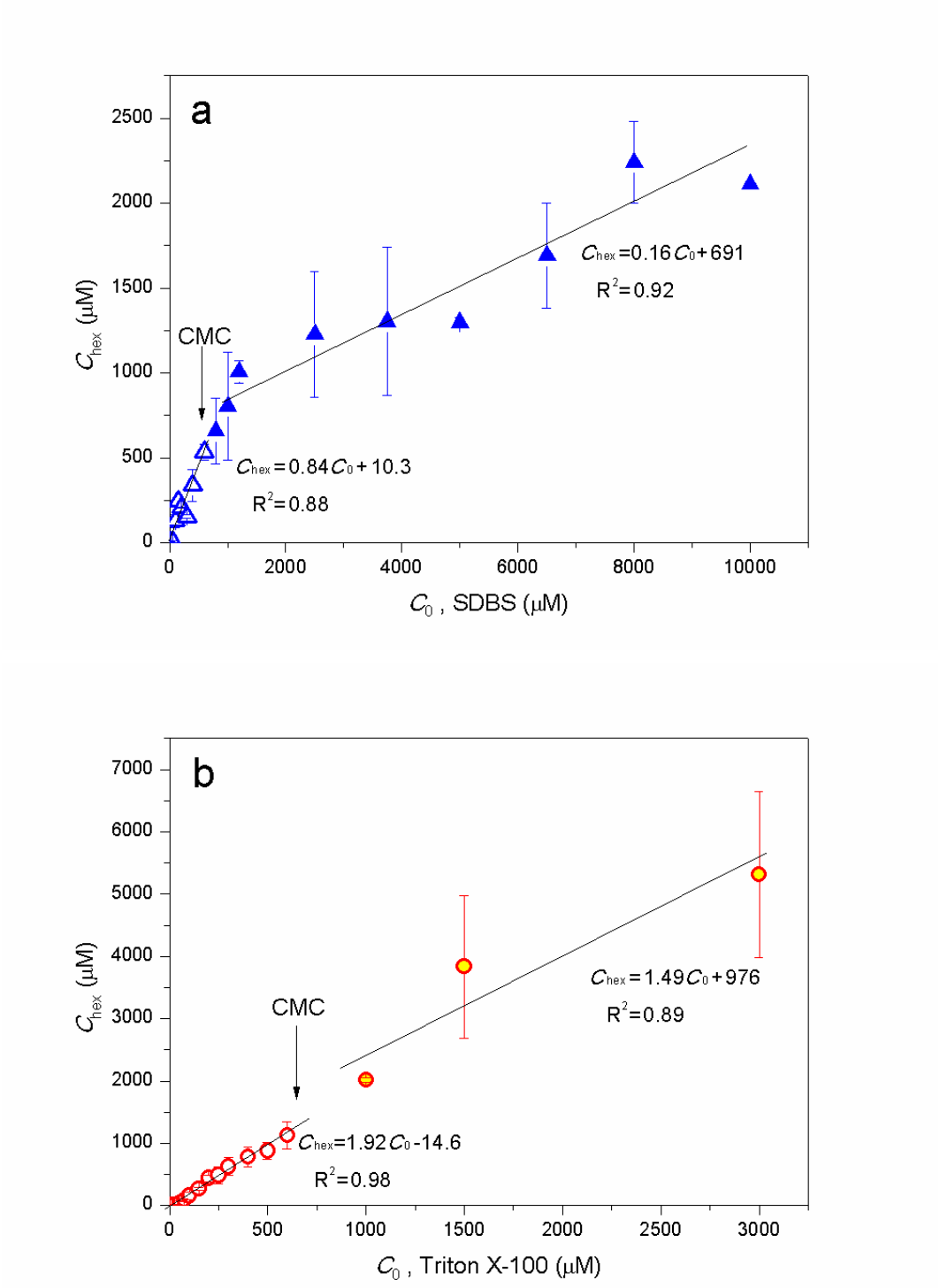


Figure 3

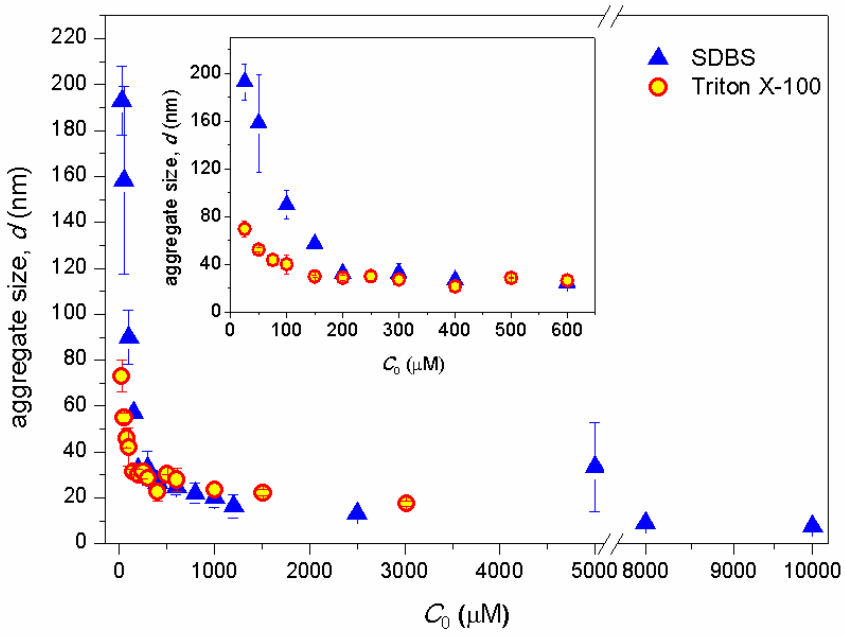


Figure 4

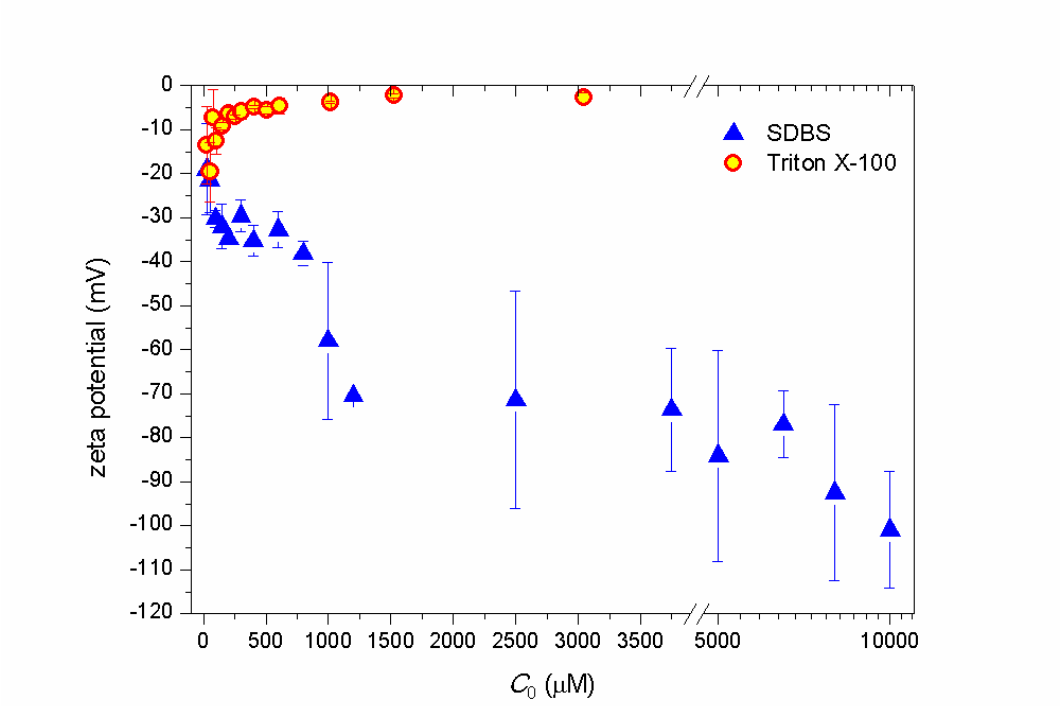


Figure 5

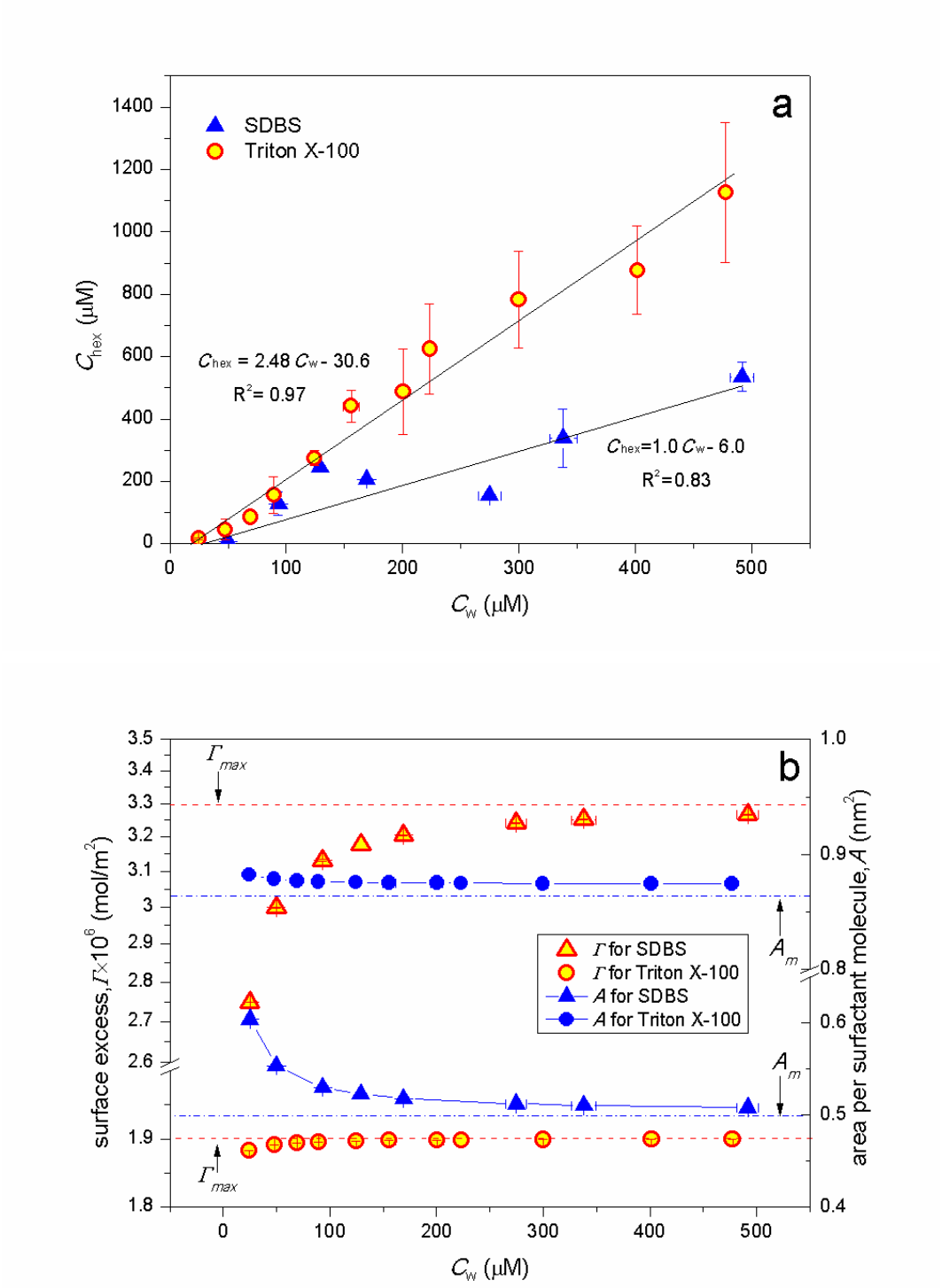


Figure 6

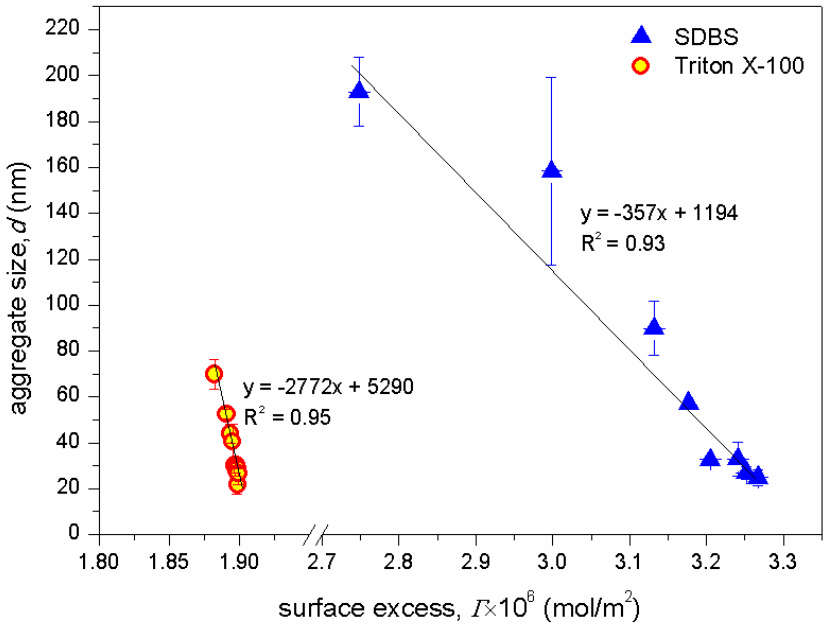


Figure 7

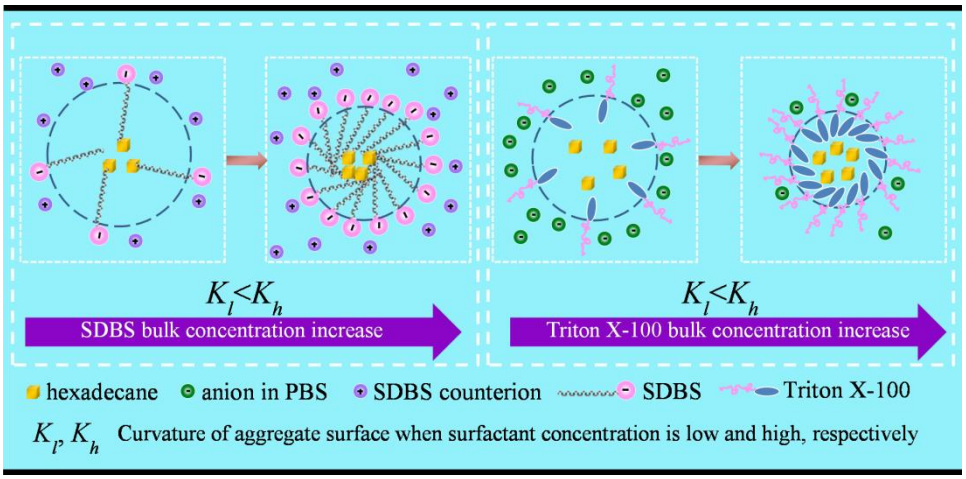


Figure 8