Ultrasonic transformation of micelle structures: Effect of frequency and power

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A comprehensive investigation on the effect of ultrasonic frequency and power on the structural transformation of CTABr/NaSal micelles has been carried out. Sonication of this micelle system at various ultrasonic frequencies and power resulted in the formation and separation of two types of micelles. High viscoelastic threadlike micelles of ~2 nm in diameter and several μm in length and tubular micelles possessing a viscosity slightly above that of water with ~30–50 nm diameter and few hundred nm length. The structural transformation of micelles was induced by the shear forces generated during acoustic cavitation. At a fixed acoustic power of 40 W, the structural transformation was found to decrease from 211 to 647 kHz frequency due to the decreasing shear forces generated, as evidenced by rheological measurements and cryo-TEM images. At 355 kHz, an increase in the structural transformation was observed with an increase in acoustic power. These findings provide a knowledge base that could be useful for the manipulation of viscosity of micelles that may have applications in oil industry.

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1. Introduction

Surfactants in the form of micelles are widely used in enhanced oil recovery (EOR) [1–5]. Oil recovery in oil drilling industry is usually carried out by flooding the reservoir with gas or water in order to flush out the oil by pressure [6]. However, this method is rather ineffective due to the difficulties in recovering oil trapped in the cracks of rocks [6]. Various methods have been introduced to increase oil recovery, such as gas injection [7], hydrocarbon displacement [8], microbial injection [9], and other methods [10–12]. The main advantage of these techniques is to reduce interfacial tension between water and oil to improve oil displacement and increase water/oil mobility, therefore increasing the amount of oil recovered [5,13,14]. One of the propitious methods is the EOR method, or also known as the third improved recovery process. Surfactant micelles are used in EOR due to their ability to form viscoelastic solution upon the introduction of “additive” or co-surfactant and fully revert back to water-like solution upon the introduction of a “breaker” [4,5,15–17].

Micelles first came into attention in 1913 when sodium palmitate solution aggregated and showed abnormal mechanical viscosity yet still possessed good electrical conductivity, therefore originally termed as “colloidal ion” [18]. Not long after, another type of pure colloidal surfactant system, sodium oleate was found to exhibit three phases of viscoelasticity at its high concentration level [19]. About 40 years later, a big discovery came to surface when the ability to trigger viscoelasticity was observed even at low micelle concentrations with the introduction of specific additives, e.g., substituted benzoic acid [20]. This induced viscoelasticity does not simply increase with increasing amounts of additive. Instead, an optimum ratio between surfactant and additive was found to be very important which is dependent upon the nature of surfactants and additives used [21–23]. Such behavior suggests that the surfactant–counterion interaction is crucial in understanding or predicting the preferred micelle structural changes. Further introduction of additive after the optimum surfactant–counterion ratio reduces its viscoelasticity due to the micelles’ structural transformation from long wormlike micelles to branched micelles or vesicles [23,24]. Micelles’ flexible aggregational response toward such stimulus offers huge potential in industrial applications and technological advancements.

There are many reports available on stimuli-induced structural transformation of micelles [24–28]. In 1996, a common type of micelle, cetyltrimethylammonium-hydroxynaphthalene-carboxylate was found to form vesicle at room temperature with a viscosity almost similar to water [25]. Upon temperature increment,
transformation of the vesicles to wormlike micelles took place, henceforth the viscoelastic appearance at high temperature [25]. Similarly, the micelle was also reported to be responding to shear [26]. This is evidence by the structural transformation from vesicle to wormlike micelle consequent to shearing [26]. In 2003, a series of polymer micelles; sodium 2-acrylamido-2-methyl-1-propanesulfonate, N-isopropylacrylamide and cinnamoyloxyethylmethacrylate were found to undergo structural growth upon UV exposure at 280 nm [27]. Such effect is due to the photodimerization of cinnamoyl chromophores, leading to photo-crosslinking of the micelles [27]. Shortly thereafter, a pH responsive micelle system was discovered. In alkaline condition, poly-(acrylic acid)45%–block-poly(N,N-diethylacrylamide)60% form crew-cut micelle but in acidic condition, it transforms to inverse star-like micelle [28]. Albeit the discovery of many active stimuli in micelle structural transformation, the mechanism involved is still vague. Recently, the wormlike structure of cetyltrimethylammonium bromide/sodium salicylate (CTABr/NaSal) micelle was found to undergo concurrent transformation to: (i) much longer and aligned threadlike micelle with much higher viscoelasticity and (ii) vesicles [29] when subjected to sonication. These two coexistent micelles can be easily separated and are stable for over a year. We reported that the shear forces generated during acoustic cavitation could induce structural changes in CTABr/NaSal micelle system [29]. The transformations to threadlike and vesicle-type micelle structures upon exposure to the soundwaves [29] were explained according to the reptation reaction theory [30,31]. Our previous study was limited to a single frequency (211 kHz) system.

In this study, we intend to (i) expand the knowledge base on the effect of ultrasound to control micelle structures by expanding the experimental scope of the ultrasonic parameters and (ii) attest the mechanism proposed when a wider range of acoustic parameters are used. Our curiosity is mostly steered by the merits and flaws of EOR technology and the potential of such micelle system to attain cleaner and environmental friendly procedures in oil recovery. In EOR, additives such as in sulfonated surfactant are commonly used trigger for changing viscoelasticity [32,33], and breakers such as chlorinated hydrocarbon compound are used to increase mobility [32]. Unfortunately, these two compounds are detrimental to the environment [32]. When sulfonate mixes with crude oil, the solubility of the toxic compounds is increased [34,35], meanwhile the introduction of chlorinated hydrocarbon breaker is considered hazardous to humans and aquatic organisms [32]. We trust that adopting such ultrasonic responsive micelle systems to EOR may eliminate the need of additional chemicals, therefore a meticulous study and authentication is vital. While we have not tested this hypothesis by experimental trials in EOR, we anticipate that oil industry will be interested in such outcomes. The results discussed in this manuscript will also attract the attention of chemists and engineers in the field of oil recovery to explore the advantages of ultrasound induced structural changes to micelle systems.

2. Experimental details

Cetyltrimethylammonium bromide (CTABr) (99%) and sodium salicylate (NaSal) (99.5%) used in this study were of the highest purity available from Sigma Aldrich. Solutions containing 15 mM cetyltrimethylammonium bromide (CTABr) and 15 mM NaSal were prepared using MilliQ purified water. All solutions were prepared fresh and left overnight to equilibrate before sonication. The total volume of the solution sonicated was 200 mL for each experiment. The sonication experiments were carried out using either a Branson 20 kHz unit or a ELAC RF generator combined with an Allied Signal plate transducers. Two types of transducers were used – horn-type transducer for 20 kHz frequency and plate transducers for 211, 355 and 647 kHz frequencies. The applied powers were also varied from 10 to 70 W. A thermostated water jacket was used for all experiments to control the temperature at 30 °C.

H₂O₂ yield was measured for all experimental settings using pure water [36,37]. The images of the sonicated samples were then taken using the cryo-TEM Transmission Electron Microscope (Tecnai, Heindoven, NL) whilst the rheological measurements were carried out using the AR-G2 Controlled Stress Rheometer from Anton Paar.

3. Results and discussion

A micelle system prepared by the ion exchange process between a charged micelle and its counterion is known to respond to various stimuli by changing its microstructures [38–40]. This relies primarily on the interference to the thermodynamic stability of the aggregational structures in the presence of the external stimuli. An example of the extensively studied micelle system is a mixture of CTABr and NaSal [41–43]. Its flexibility in forming different aggregational structures makes it a promising material for many applications in industries. The aggregational microstructures rely highly upon the concentration ratios of these two components. No other factors were reported to significantly change its structure until our recent report on the effect of ultrasound (US) on CTABr/NaSal micelle system [29]. In this study, a 1:1 mixture of CTABr (15 mM) and NaSal (15 mM) was found to form entangled wormlike micelle (WLM). The solution was then sonicated at 211 kHz frequency, 40 W and maintained at 30 °C. The transformation to threadlike micelle (TLM) and tubular micelle (TM) were observed by cryo-TEM imaging and rheological measurements. This aggregational alteration starts immediately upon sonication and could be visibly monitored throughout sonication (Fig. 1).

The micelle structural transformation is easily reflected by its degree of viscoelasticity due to the molecular rearrangement between different micelle structures [29]. Rheological measurement is one of the best methods to follow the extent of the structural transformation. As per our previous report, the long TLM (top layer) was found to be approximately 4 times more viscoelastic than the WLM before sonication. On the other hand, the TM (bottom layer) was found to possess viscosity almost similar to that of water. The transformed structure was irreversible upon heating [29]. This is an advantage to EOR process as the surfactant will not lose its surface activity at the high temperature conditions in the reservoir [14]. Losing its surface activity results in decreasing efficiency in oil recovery [14]. Therefore, the ability of US to cater this reaction may be a breakthrough for applications in industries such as EOR and need to be understood well. For this reason, experiments with varying sonication parameters, viz., a range of ultrasonic frequency at the same power, and with horn and plate type transducers, were carried out in order to expand the knowledge base. The power was fixed at 40 W and the temperature was maintained at 30 °C. The images and the viscosity values of the final solution are shown in Fig. 2.

20 kHz sonication was carried out using an ultrasonic horn with a 1 cm diameter tip placed in the solution. This type of reactor is commonly used for homogenization process due to its strong shear forces and low radical production. As seen in Fig. 2(a)(i), there is no separation in the final sonicated sample and the rheological

Fig. 1. The visible sonication time dependent changes of CTABr/NaSal system.
measurement showed a decrease in its viscosity to 3.3 Pa s, about half of the value before sonication (6.2 Pa s). The decrease is due to the breakage of WM by the strong shear forces generated during acoustic cavitaton.

As can be seen from Fig. 2(a)(ii–iv), sonication of CTABr/NaSal at 211, 355 and 647 kHz results in the formation of two types of micelle solutions with opposing degree of viscoelasticity. These two systems form separable layers and stay unmixed even after the sonication is stopped. The top layer shows a very high viscosity when compared to the control solution, whilst the bottom posses viscoelasticity just slightly above water. This is confirmed by the viscosity values as shown in Fig. 2(b). The viscosities of the top layers are 24.7 Pa s for 211 kHz, 17.2 Pa s for 355 kHz and 12 Pa s for 647 kHz. The viscosity values for the bottom layers are 0.03 Pa s for 211 kHz, 0.9 Pa s for 355 kHz and 2.0 Pa s for 647 kHz. Detailed examination of the viscosity values for the top layer reveals a clear decreasing viscosity trend with increasing frequency. On the contrary, an increasing viscosity was observed with increasing frequency for the bottom layer. To understand this, three crucial elements need to be understood: (i) the micelle structures formed in both layers, (ii) the mechanism involved in the transformations and (iii) the physical and chemical effects of sonication with increasing US frequency.

The images for the micelle systems characterized by cryo-TEM for both top and bottom layers for sonication at 211, 355 and 647 kHz are shown in Fig. 3. Very long TLM structures were observed in the top layer for all three frequencies. They are ~2 nm in diameter and several μm in length. The TLM in all three systems seem to possess some alignment. The alignment observed was confirmed to be due to the effect of sonication and not due to other factors involved during cryo-TEM sample preparation [29]. This is supported by the WM entanglement structure observed in the cryo-TEM image of CTABr/NaSal system prior to sonication [Supporting Information in Ref. 29], even though it was prepared and examined under a similar cryo-TEM process. The TLM seems to be most aligned at 211 kHz and gets less coordinated with increasing frequency. A detailed discussion of the TLM formation at 211 kHz has been provided in our previous report [29]. A brief discussion on the mechanism is provided later.

The cryo-TEM images for the bottom layers show the existence of mainly tubular micelles (TM), which are ~30–50 nm diameter and few hundred nm length. The diameter seems to increase with the increasing frequency. In fact, at 211 kHz, despite the formation of the tubular micelle structure, the spherical shape of vesicles is still visible, although not very clear. This is due to their inability to fully revert back to a tubular structure after shear is applied by the blotting process during cryo-TEM sample preparation [29]. In other words, the micelle system forms a more stable tubular structure when sonicated at higher frequency. This also indicates that the coalesced vesicles as observed at 211 kHz are intermediates rather than stable structures [29,44]. This also explains the increasing trend of the viscosity measured for the bottom layers with the increasing US frequency. T-shaped and Y-shaped junctions on the tubular micelles were also discussed in our previous report [29]. These are the point of interactions between vesicles in forming the TM [29,45].

In order to appreciate the potential use of ultrasound to control such structural transformations, an understanding of the mechanism involved is necessary. The transformation of WM to TLM and TM that occurs upon sonication can be divided to three stages: (i) reptation of the micelle from the WM entanglement, (ii) end to end reaction between WM micelles and (iii) separation of the two different viscoelasticity of micelle layers [29,31]. Stages (i) and (ii) are based on the well known extended version of the reptation reaction theory [30]. The reptation process is catered by oscillating micro bubbles in the solution, in particular the ones that are trapped in between micelles’ entanglement [29]. These microbubbles posses a higher stability due to them being trapped in between WMs [29]. When the micelle reptated free, the microbubbles lose their stability and implode [29]. The implosion results in the release of energy in the form of a temperature jump in the surrounding solution [29]. This energy causes the end to end reaction to occur, emanating in the formation of longer TLM [29,31]. These two major effects of sonication, viz., shear from oscillating microbubbles and the temperature jump from bubble’s implosion are responsible for the structural transformations in micelles [29].

The next step is to understand the effect of frequency. Sonication results in the formation of oscillating microbubbles at the antinodes. The wavelength varies with ultrasonic frequency – longer at low frequency and shorter at high frequency. This induces the formation of larger microbubbles at low frequency when compared to those at higher frequencies. The oscillation of larger microbubbles results in the generation of relatively higher shear. As the frequency increases, microbubbles in the antinodes get smaller and...
generate relatively lower shear. Therefore, the shear decreases with increasing sonication frequency. According to the mechanism, the reptation of WM is promoted by shear from the oscillating micelles. It seems logical that the TLM is the longest and most abundant at 211 kHz with highest viscoelasticity. This agrees with the TEM images and rheological measurement as shown in Figs. 2 and 3. To support the argument that the shear forces play a major role in causing changes to the structures and viscosity, another set of experiment was performed at a fixed frequency (355 kHz) but increasing power from 10 to 70 W. The shear is known to increase with increasing power (bubble size increases with an increase in power). It can be expected that an increase in the micelle transformation from WM to TLM occurs with increasing power. The result of this experiment is shown in Fig. 4.

The shear forces generated at 10 W did not generate any structural changes in micelles. Sonication at 40 and 70 W results in the transformation of WM to TLM and TM as observed before. The viscosity increases with the increasing power. This supports the significant effect of shear in the formation of TLM from WM upon sonication. The viscosity of the bottom layers did not show a significant change with increasing power from 40 W to 70 W. The recombinations of micelles in forming LTM and TM, as well as the separation of these two structures were discussed in detail in our previous reported [29].

4. Conclusion

A comprehensive study on the effect of ultrasonics on micelles’ microstructural transformation is reported. When sonicated at a fixed 40 W power and increasing frequencies from 211 to 647 kHz, the wormlike micelles transformed to long threadlike micelles and tubular micelles simultaneously. Such structural transformations were studied by cryo-TEM and rheological measurements. Similar observation was visible when the micelle solution was sonicated at fixed 355 kHz frequency and increasing power from 10 to 70 W. Rheological data revealed an increasing viscosity trend for long threadlike micelle, but the viscosity values for tubular micelle were not affected with increasing sonication power. The viscoelastic long threadlike micelles formed are stable over months. We believe that ultrasonic modification of micelle structures is a promising method that may have potential industrial applications especially in enhanced oil recovery.

Acknowledgements

The authors acknowledge Eric Hanssen from the Advanced Microscopy Facility at the Bio 21 Institute. N.S.M.Y. also thanks SLAI/Bright Sparks scholarship and grant UM.C/HIR/MOHE/SC/07 from the University of Malaya.

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