OC-29: Ultrasound-Induced Changes to Micelle Structures

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The growth of micelles is found to be effectively promoted in the presence of aromatic anionic counterions such as salicylates (Shukla and Rehage, 2008), tosylates (Rao, 1987), mono- and disubstituted halobenzoates (Shukla and Rehage, 2008; Lu et. al., 1998) as well as methylbenzoates (Qi and Zakin, 2002). These studies suggest that apart from the responsiveness of the surfactant itself, the nature of counterions in ionic micelle systems can also cause spectacular effects on the evolution of micellar morphology, which consists of spherical, rodlike, wormlike, linear, entangled and branched/interconnected micelles. (Magid, 1998) A simple illustration of structural changes is shown in Figure 1.

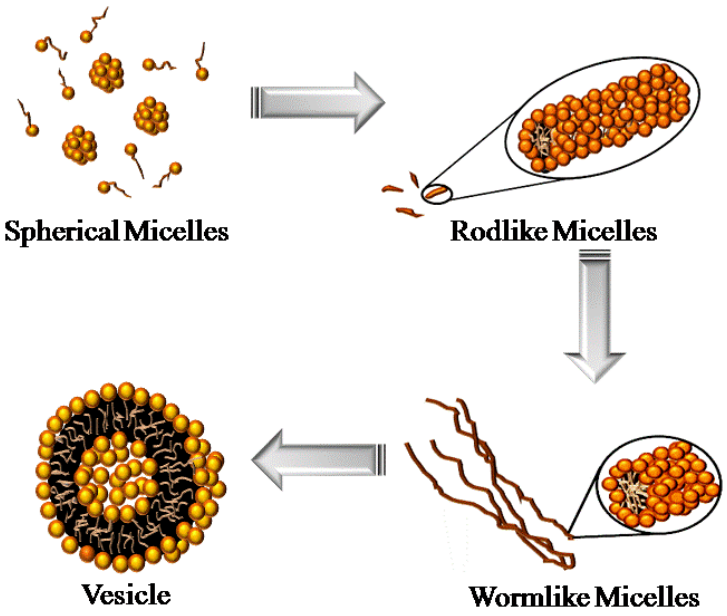

Figure 1. An illustration of the increasing degree of micelle growth from spherical micelles to vesicles under the influence of a stimulus such as pH and temperature.

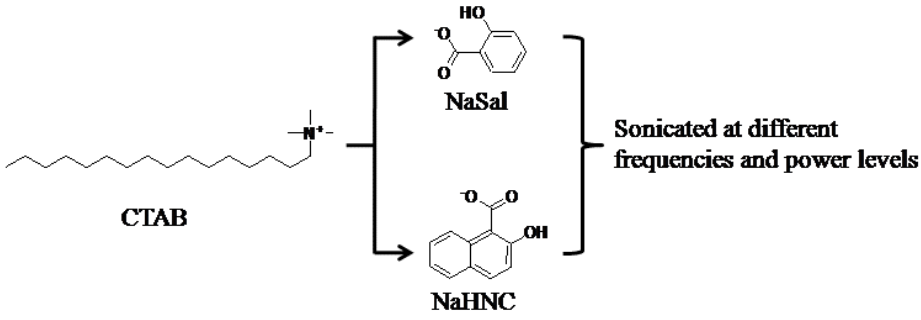

Figure 2. The molecular structures of CTAB, NaSal and NaHNC used in the system. CTAB/NaSal and CTAB/NaHNC systems were sonicated at different frequencies and power levels with and without temperature control in order to explore the sonication induced structural changes.

The morphological variations in micelles are crucial to cater many applications including drug delivery. The structural changes of micelles may be induced by different means of stimuli (Cohen, 2010; Zhao, 2009) including ultrasound (Wang, et al., 2007). An added effect of ultrasonication to the changes in the morphology of micelles is that

the structural change may lead to the release of encapsulated drugs in micelle-based drug delivery systems (Husseini and Pitt, 2009). Despite potential applications of ultrasound induced structural changes to micellar systems, studies involving ultrasonic modification of micellar structures are scarce. While the effect of ultrasound on the modification of micellar structure was reported earlier (Wang, et al., 2007), the mechanistic details are not discussed in detail. It is well known that sonication of a liquid medium induces acoustic cavitation under certain experimental conditions. Both chemical and physical effects are generated by acoustic cavitation (Ashokkumar and Mason, 2007). Whether the chemical or physical or both effects are responsible for the observed structural changes to micellar systems has not been explored. In this study, cetyltrimethylammonium bromide (CTAB) micelles with two different counterions, sodium salicylate (NaSal) and sodium hydroxynaphthalene carboxylate (NaHNC) were sonicated at different frequencies (20 kHz – 1 MHz) and power levels with and without temperature control (Figure 2).

In general, the viscosity decreases upon sonication for CTAB/NaSal system. From HPLC and mass spectrometry data, it is observed that the sonication of NaSal itself results in the degradation of the compound forming hydrophilic products. The counterion with more hydrophilic property does not penetrate deep into the micelle layer leading to structural changes in the micelle. A substantial increase in the viscosity of CTAB/NaHNC upon sonication was observed, indicating the growth of micelle structure due to the increasing binding of the counterion. Such effect was observed by heat on erucyl bis-hydroxyethyl)methylammonium chloride (EHAC)/NaHNC micelle system (Kalur et al., 2005). The sonication of CTAB/NaHNC system at 20 kHz under temperature controlled condition indicated the occurrence of similar structural changes. This suggests that other than the effect of heat generated upon sonication on the micelle system, the shear forces generated by 20 kHz sonication play a major role in inducing micelle structural changes. Further discussion on the effect of sonication of the micellar system at higher frequencies and different power levels will be discussed.

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