

# STRUCTURES AND DYNAMIC VISCOELASTIC PROPERTIES OF MICELLES OF MIXTURES OF SURFACTIN WITH CATIONIC SURFACTANT IN AQUEOUS SOLUTION

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Surfactin sodium salt (SFNa) consisting of a long alkyl chain and cyclic peptide is a biosurfactant produced by *Bacillus subtilis*. SFNa is expected to be a useful material in cosmetics, medical field, and so on because it shows unique surface activities such as significant reduction of surface tension at extremely dilute concentration. In our previous study, we found SF formed monodisperse spherical micelles with low aggregation number in aqueous solution [1]. In addition, the aggregation number of SF micelles was discretely changed with varying salt concentration. However, such small changes of micelle structures cause slight change in viscoelasticity of the micelle solution. In the case that SF is used in detergent, tuning viscoelastic properties of its solution is requested. To tune the viscoelastic properties, tuning the structures of micelles should be important. Mixing of anionic and cationic surfactant is one of the effective method to tune the structures of micelles. Therefore, addition of a cationic surfactant to anionic SFNa is expected to cause drastic change in viscoelastic properties owing to structural changes of SF micelles. Thus, in this study, we investigate the structures of micelles consisting of anionic SFNa and cetyltrimethyl ammonium bromide (CTAB) as a cationic surfactant and their viscoelasticity related to the structures of micelles. SFNa was provided by Kaneka Corporation and CTAB was dissolved at desired surfactant concentration, mole fraction of SFNa ( $X_{SF}$ ) and ratio of cation to anion (C/A) in aqueous NaCl solution. For the resulting SFNa-CTAB micelle solutions, visual observation, small angle X-ray scattering (SAXS) and dynamic viscoelastic analyses measurements were performed. We found that viscosity of aqueous solutions of SFNa-CTAB micelles are increased with increasing SF content in  $X_{SF} < 0.2$  and CTAB content in  $0.65 < X_{SF}$ . Therefore, it should be considered that structures of mixed micelles in these regions are much different from those of SFNa or CTAB micelles.

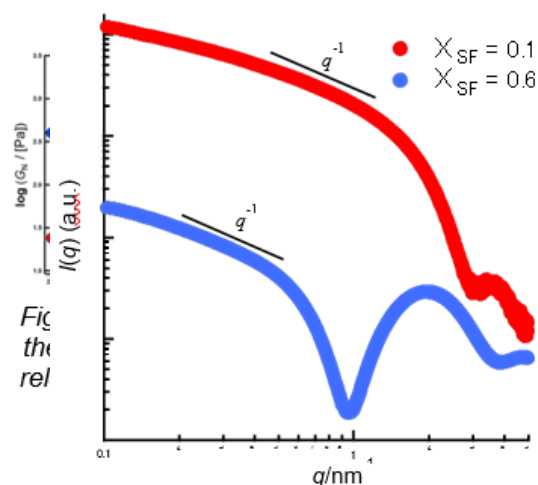


Figure 1 – SAXS profiles of SFNa-CTAB micelles at  $X_{SF} = 0.1$  (Red) and  $0.6$  (Blue).

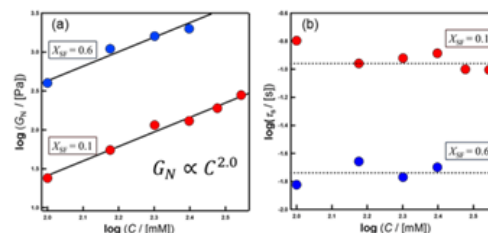


Figure 2 – concentration dependences of (a) the plateau moduli ( $G_N$ ) and (b) the terminal relaxation times ( $\tau_s$ ) of SFNa-CTAB micelles at  $X_{SF} = 0.1$  (Red) and  $0.6$  (Blue).

Figure 1 shows SAXS profiles of SF-CTAB micelles at  $X_{SF} = 0.1$  (Red) and  $0.6$  (Blue). It could be confirmed scattering intensities in both systems are proportional to  $q^{-1}$  at low  $q$  range. Therefore, SF-CTAB mixtures form worm-like micelles at  $X_{SF} = 0.1$  and  $0.6$ . However, SAXS profiles of these micelles are much different in high  $q$  region. Consequently, these micelles have different interiors. Thus, to investigate the effect of such structural difference of micelles on viscoelastic properties, dynamic viscoelastic measurements were performed. Figure 2 shows concentration dependences of the terminal relaxation times ( $\tau_s$ ) of SFNa-CTAB micelles at  $X_{SF} = 0.1$  and  $0.6$  obtained from the analyses for frequency dependence of storage and loss moduli by using Maxwell model. The  $\tau_s$ s of these micelles are almost constant against micelle concentrations. This result means the entanglements of worm-like micelles of SFNa-CTAB mixtures are regarded as transient networks.

## References

1. Fujii, S. et al., Scientific Reports 2017, 7, 44494.
2. Naruse, K. et al., J. Phys. Chem. B. 2009, 113, 10222-10229