# 3P1-7

# Detailed investigations of oscillation and relaxation behaviors in threadlike micelle by means of ultrasonically induced birefringence

超超音波誘起複屈折法における紐状ミセル水溶液の振動・緩和挙動の詳細な解析

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## 1. Introduction

In aqueous solutions of cetyltrimethylammonium bromide (CTAB) and sodium salicylate (NaSal), so called worm-like micelles are formed. Their rheological behaviors strongly depends on CTAB concentration ($C_D$) and NaSal concentration ($C_S$).[1,2] Shikata and co-workers discussed rheological properties using $C_D$ and excess salt concentration $C_S^* = C_S - C_D$ in the case of $C_S > C_D$.[1,2] Yasuda and co-workers observed the damping oscillation in the ultrasonically induced birefringence in the solutions at the condition at $C_S < C_D$ and discussed relation of period of oscillation and plateau shear modulus.[3,4] Matsuoka and Matsuda observed relaxation components in birefringence signal after damping oscillation is disappeared in the condition at $C_S > C_D$.[5] However, concentration range was limited for observation of relaxation components. In this study, we investigate concentration dependence of damping oscillation and relaxation in the ultrasonically induced birefringence in aqueous solution of CTAB and NaSal at various concentrations and discuss their behaviors in detail.

## 2. Experimental

CTAB was purchased from Tokyo Chemical Industry. CTAB was purified by recrystallization and dried in vacuum. NaSal was supplied from Wako Pure Chemical industries and used after drying in vacuum. Ultrasonic induced birefringence method was based on the literature.[3,4] Burst wave width is 8 s is used for observation damping oscillation measurements and it is 20 s for relaxation time measurements. For analysis of relaxation time, we used the birefringence data after oscillation is disappeared and the data are fitted by a simple exponential decay function. All measurements are carried out at 25 °C.

## 3. Results and Discussion

Figure 1 shows a transient signal of ultrasonically induced birefringence in aqueous solutions of CTAB and NaSal at $C_D$ = 20 mM and $C_S^*$ = 40 mM. Relaxation of birefringence is clearly observed after oscillation is dissipated around 1.5 s.

Damped oscillation of birefringence in Fig. 1 indicates that oscillation does not consist of a single frequency component. We carried out fast

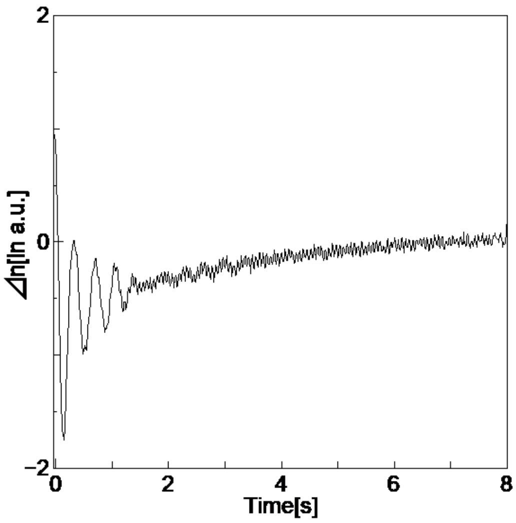


Fig.1 Transient ultrasonically induced birefringence in aqueous solution of CTAB and NaSal ($C_D$ = 20mM, $C_S^*$ = 40mM)

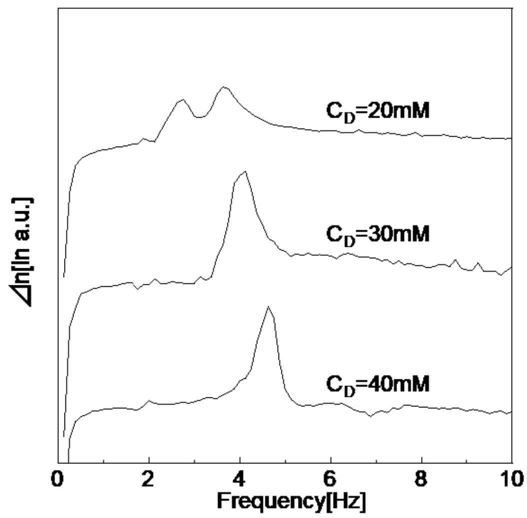


Fig.2 Frequency spectra of ultrasonically induced birefringence obtained by Fast Fourier Transform (FFT) ($C_S^*$ = 40mM)

Fourier transform (FFT) to obtain frequency spectra of birefringence.

The real part of frequency spectra at $C_D = 20$, 30, 40 mM and $C_S^* = 40$ mM are shown in Fig. 2. Two distinct peaks are observed at $C_D = 20$ mM. In case that $C_D = 30$ mM, two different peaks which have almost the same peak frequency are superimposed. At $C_D = 40$ mM, only one peak is observed.

CTAB concentration dependences of peak frequency with different $C_S^*$ are shown in Fig. 3. The peak frequency is not influenced by $C_S^*$. Linear relationship between $C_D$ and the peak frequency if we adapt the lower peak frequency at $C_D = 20$ mM. Although proportional dependence between $C_D$ and the peak frequency is expected from concentration dependence of plateau shear modulus[1,2] and relation period of oscillation with shear modulus[4], proportional dependence between $C_D$ and the peak frequency is not observed.

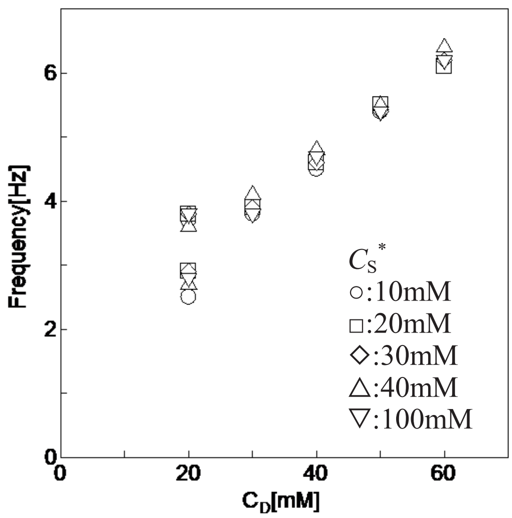


Fig.3 $C_D$ dependence of peak frequency at various $C_S^*$

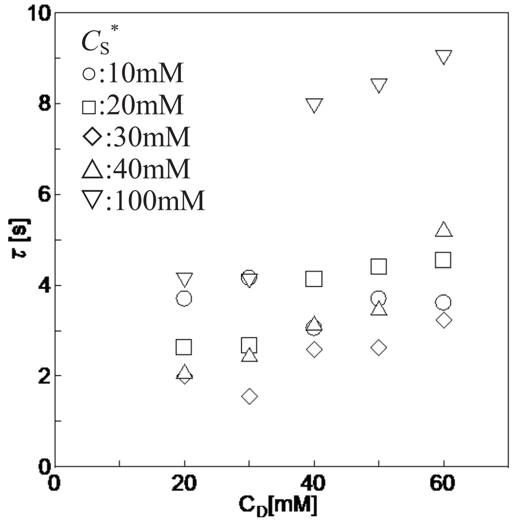


Fig.4 $C_D$ dependence of relaxation at various $C_S^*$

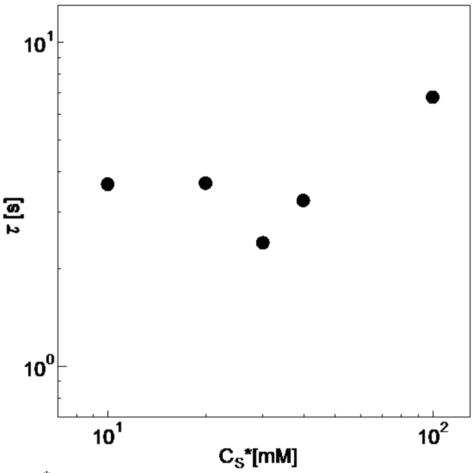


Fig.5 $C_S^*$ dependence of relaxation time averaged over various $C_D$ concentration

CTAB concentration dependences of relaxation time with different $C_S^*$ are shown in Fig. 4. In Fig. 4, the gap in relaxation time is observed between at $C_D$=30 mM and 40 mM.

Relaxation time depends both $C_D$ and $C_S^*$. The averaged value of relaxation time over different $C_D$ are plotted against $C_S^*$ and it is shown in Fig. 5. Relaxation time takes minimum at $C_S^*$=30 mM. This tendency agreement with that of relaxation time obtained by Rheological measurements.[2] However, relaxation time obtained by birefringence depends both $C_D$ and $C_S^*$, while relaxation time of rheological measurements only depends on $C_S$*.[1,2] Relaxation time of ultrasonically birefringence reflects relaxation related to the orientational order. The origin of relaxation time may differ from that of rheological one.

In this work, we carried out detained investigation of damping oscillation and relaxation in worm-like micelle in aqueous solution of CTAB and NaSal. Critical behaviors are observed for both cases. Further investigations are required to elucidate behaviors observed in this work.

**References**

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