

Rapid Molecular Motion in Long Threadlike Micelles

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Because a micelle is constituted by rather weak hydrophobic intermolecular interaction, molecular motion in the micelle is quite active and quick. This rapid molecular motion in a long threadlike micelle formed in an aqueous solution of a cationic detergent, cetyltrimethylammonium bromide (CTAB), with sodium salicylate (NaSal), was examined by dielectric relaxation analysis. We found broadly distributed dielectric spectra in the frequency range from 10^6 to 10^9 s⁻¹ due to molecular motion of micelle-forming molecules, which were proportional in magnitude to the concentration of CTAB. The fastest relaxation mode, around 10^9 s⁻¹, is attributed to the rotation of an ionic pair formed by a headgroup of a cetyltrimethylammonium cation, CTA⁺, and a salicylate anion, Sal⁻, as observed in the spherical micelle of CTAB in aqueous solution. On the other hand, a slow relaxation mode, around 10^7 s⁻¹, is caused by the localized distribution of ions, CTA⁺ and Sal⁻, in the threadlike micelle after the lifetime of the ionic pair.

Introduction

Detergents form micelles in aqueous solutions above their critical micelle concentrations. A micelle in an aqueous solution, which is well-known as one of the simplest molecular assemblies, has several kinds of shapes¹ such as spherical, rodlike or long threadlike, disklike, and so on. The shape of a micelle depends on the species of the detergent and the presence of additives. For example, cetyltrimethylammonium bromide (CTAB) forms spherical micelles in pure water. However, it forms long threadlike micelles in aqueous solution with aromatic salts such as sodium salicylate (NaSal) at the molar concentration equal to or higher than that of CTAB.^{2,3} Because a micelle has no specific strong intermolecular interaction between two detergents as DNA has specific intermolecular hydrogen bonds between two pairs of residues, Adenine–Guanine and Thymine–Cytosine, detergents can move and rotate fairly freely in the micelle. A threadlike micelle is recognized as being a highly flexible threadlike material from its mechanical or rheological behavior.⁴ The cause of its high flexibility might be the quick molecular motion of micelle-forming detergents and additives.

Dielectric relaxation analysis (DRA) is conventional, but quite sensitive to the presence of electric dipole moments in systems examined. DRA is also quite useful for investigating the rate of motion for molecules with dipole moments, since it detects the electric capacitance and conductance as a function of frequency (ω) of an applied sinusoidal electric field.^{5,6} A micelle formed by ionic detergents in an aqueous solution possesses several kinds of dipole moments, which are possibly investigated with DRA. For example, in a spherical micelle formed by CTAB, ionic pairs consisting of a cationic headgroup of CTA⁺ and a bromide anion (Br⁻) are generated. This ionic pair behaves as a relaxing dipole moment because of rotational molecular motion. DRA detected a relaxation mode with strength proportional to the molar concentration (C_D) of CTAB caused by the rotation of ionic pairs at $\omega \sim 2 \times 10^9$ s⁻¹.^{7,8} In this study, we apply DRA to the investigation into the molecular motion of

micelle-forming substances in a long threadlike micelle formed in an aqueous CTAB and NaSal solution (CTAB:NaSal/W).

Experimental Section

Materials. Cationic surfactant, cetyltrimethylammonium bromide (CTAB), was purchased from Wako Pure Chemicals Ltd. (Osaka, Japan) and was purified twice by recrystallization with mixed solvents of methanol and acetone. Special grade sodium salicylate (NaSal) and sodium bromide (NaBr) were purchased from the same company and were used without any further purification. Highly deionized water with specific resistance more than 16 M Ω cm⁻¹ was obtained with a Milli Q SP system (Millipore).

Methods. The electric conductance (G) and capacitance (C) of samples were measured using an RF impedance analyzer (Hewlett-Packard, HP4191A) equipped with a homemade electrode cell⁸ at room temperature (25 °C) in the ω range from 6.28×10^6 to 6.28×10^9 s⁻¹. On the other hand, in the ω range lower than 6.28×10^6 s⁻¹, a precision LCR meter (Hewlett-Packard, HP4282A) was used to determine G and C with an electrode cell possessing variable-distance electrodes and a water circulating vessel for temperature control at 25 °C.

In a measurement with the LCR meter, a strong electrode polarization effect existed in the low ω range, which seriously affects the C value for samples with higher G values than a sample with $C_D = 10$ mM. In general, the effect of electrode polarization⁹ becomes stronger upon increasing the electric conductivity, and it is more difficult to evaluate the capacitance exactly as the material constant of an examined sample. One of the most effective factors governing the strength of the electrode polarization should be the high mobilities of Na⁺ and Br⁻ ions in examined solutions; therefore, the C value for a threadlike micellar system in the low ω side was estimated approximately as a difference between a C value for the micellar sample and that for an aqueous NaBr solution with a G value very similar to that of the micellar sample. The G_0 value was determined as the constant electric conductance at the low-frequency side.

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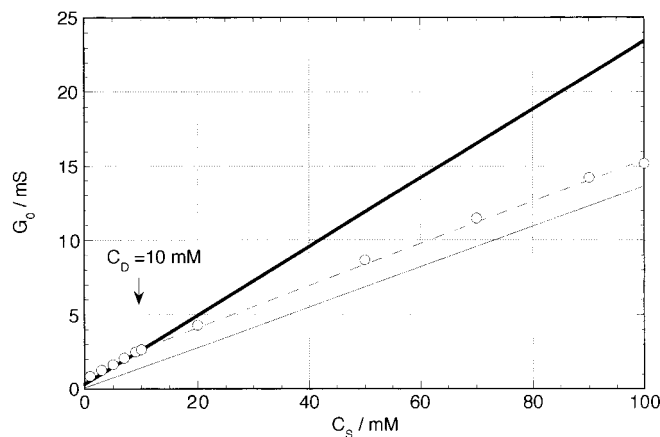


Figure 1. The dependence of the electric (direct current) conductance (G_0) on the molar concentration (C_S) of NaSal for the CTAB:NaSal/W system with the CTAB concentration (C_D) of 10 mM at room temperature (25 °C). Thick and thin solid lines represent the concentration dependence of G_0 for aqueous NaBr and NaSal solutions at the same temperature, respectively.

Results and Discussion

The formation of the threadlike micelle can be detected very easily under observation with eyes, because the viscosity of a sample increases steeply at the condition that the molar concentration (C_S) of NaSal is equal to C_D . When one keeps C_D constant, a dramatic change in the electric (direct current) conductance (G_0) obtained at the low ω side is observed at the onset of the threadlike micelle formation at $C_S = C_D$. Figure 1 shows a typical change in G_0 with C_S at $C_D = 10$ mM. In the condition of $C_S < C_D$, the slope of G_0 vs C_S is very similar to that of an aqueous NaBr solution (a thick solid line in Figure 1). However, above the break point at $C_S = C_D$, the slope obviously changes to a value corresponding to that of an aqueous NaSal solution (a thin solid line in Figure 1).

This means that a threadlike micelle is formed by CTA^+ and Sal^- , and the molar ratio between them is 1:1 as in a salt, CTASal. All the Br^- anions in a micelle are replaced by Sal^- anions, until a complete threadlike micelle possessing the ratio of 1:1 forms at $C_D = C_S$, then excess Sal^- anions remain in the bulk aqueous phase in the condition of $C_S > C_D$. This argument can also be made with data obtained by an NMR experiment.⁴ Consequently, the threadlike micelle of the CTAB:NaSal/W system has no electric charges, but its surface is electrically neutral. This point makes discussion on the dielectric relaxation behavior of the CTAB:NaSal/W system much simpler, because one does not have to take into account the contribution of dissociated counterions around the micelle. Therefore, the dielectric relaxation behavior for the CTAB:NaSal/W system can be caused by events which occur in a threadlike micelle.

In aqueous solutions of electrically charged colloidal particles such as polyelectrolytes and charged micelles, the fluctuation of a counterion distribution around particles is sometimes essential to the dielectric relaxation responses.^{9,10} The fluctuation of counterion distribution is able to make large, induced electric dipole moments.

We found broad dielectric relaxation spectra for the CTAB:NaSal/W threadlike micellar system, which distributed in the ω range from 10^6 to 10^9 s⁻¹. To estimate the pure contribution of a threadlike micelle to the dielectric constant, the value ($\epsilon'_w = 78$) due to the medium, water, was subtracted from the obtained ϵ' value to get an increment ($\Delta\epsilon'$) due to the micelle; $\Delta\epsilon' = \epsilon' - \epsilon'_w$. On the other hand, the contribution to the

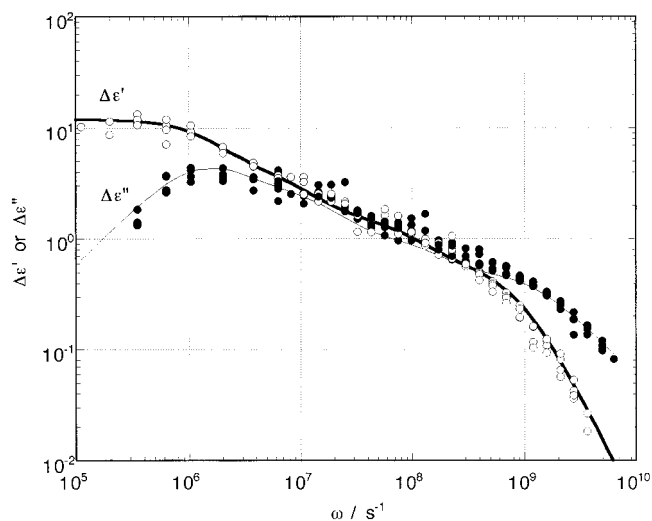


Figure 2. The relationship between the dielectric constant increment ($\Delta\epsilon'$), the loss increment ($\Delta\epsilon''$), and the frequency (ω) for the CTAB:NaSal/W threadlike micellar system with $C_D = C_S = 1, 2.5, 5$, and 10 mM at 25 °C. All the data (except for those with $C_D = 5$ mM) were shifted vertically to get the best superposition onto the data with $C_D = 5$ mM. Thick and thin solid lines mean the ω dependence of the theoretical model functions (eq 1) with the parameters in Table 1.

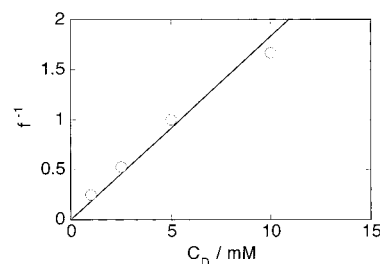


Figure 3. The relationship between the reciprocal of the shifting factors (f^{-1}) used to get Figure 2 and C_D .

dielectric loss of a micelle was estimated as an increment ($\Delta\epsilon''$) in ϵ'' : $\Delta\epsilon'' = \epsilon'' - \epsilon''_w - G_0(C_0 \omega)^{-1}$, where ϵ''_w and C_0 are the dielectric loss of water at each ω and the capacitance of a vacant electrode cell, respectively. In Figure 2 the relationship between $\Delta\epsilon'$, $\Delta\epsilon''$, and ω for the CTAB:NaSal/W systems with $C_D = C_S = 1, 2.5, 5$, and 10 mM is that they are superposed upon one another by shifting data along the ordinate taking the data for the 5 mM sample as the standard. Shifting factors used to get Figure 2 are plotted in Figure 3 as a function of C_D . One can easily recognize that the dependence of $\Delta\epsilon'$ and $\Delta\epsilon''$ on ω is independent of C_D , but the magnitudes of the spectra are essentially proportional to C_D .

In general, when a system has only one dielectric relaxation mode caused by rotational molecular motion, one finds only one maximum in $\Delta\epsilon''$ and a stepwise decrease in $\Delta\epsilon'$ at ω corresponding to the rotational relaxation rate of the molecule. In this case, $\Delta\epsilon'$ and $\Delta\epsilon''$ are described with Debye type functions.^{5,6} The solid thick and thin lines in Figure 2 represent theoretical model functions, $\Delta\epsilon'_{\text{cal}}$ and $\Delta\epsilon''_{\text{cal}}$ (eq 1), consisting of four Debye type functions with the combination of relaxation times and strength (τ_i and $\Delta\epsilon_i$, $i = 1$ to 4 summarized in Table 1) to get the best fit curves to the data.

$$\Delta\epsilon'_{\text{cal}} = \sum_{i=1}^4 \frac{\Delta\epsilon_i}{1 + \omega^2 \tau_i^2} \quad \Delta\epsilon''_{\text{cal}} = \sum_{i=1}^4 \frac{\Delta\epsilon_i \omega \tau_i}{1 + \omega^2 \tau_i^2} \quad (1)$$

Because molecular-level events in a threadlike micelle formed in the CTAB:NaSal/W system are essential to dielectric

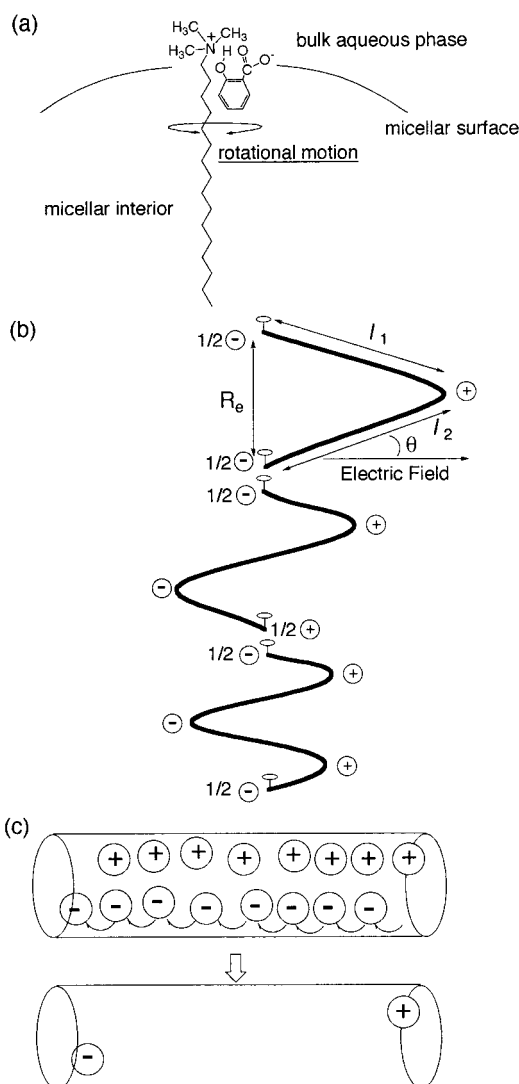


Figure 4. (a) Schematic representation for an ionic pair consisting of CTA⁺ and Sal[−] rotating in the threadlike micelle. (b) Schematic models for several types of the bending motion for threadlike materials pinned down at both terminals possessing the same contour length. Each sketch means the two-dimensional projection of a snapshot for bending conformations of a threadlike micelle between two entanglement points which could be recognized to be confined at constant spatial points in the short time region as discussed in the text. (c) A schematic model representing a mechanism for the propagation of separated charges along the threadlike micelle. In a cylinder, the separation of electric charges propagates by exchanging negative charges. Consequently, the cylinder is recognized to have an electric dipole moment as described in the bottom picture.

TABLE 1: Parameters, $\Delta\epsilon_i$ and τ_i , for eq 1 to Give the Best Fit $\Delta\epsilon'_{cal}$ and $\Delta\epsilon''_{cal}$ Curves in Figure 2

i	1	2	3	4
τ_i/ns	1.2	10	100	700
$\Delta\epsilon_i$	0.55	0.9	2.5	8

relaxation as discussed above, the proportionality between the magnitude of the dielectric spectra and C_D looks reasonable at a glance. The fastest dielectric relaxation mode, which can be described with the relaxation time of 1.2 ns in the model, is attributed to the rotational motion of an ionic pair consisting of CTA⁺ and Sal[−] in the micelle^{8,11} schematically depicted in Figure 4a, since the C_D independent rotational relaxation time of 1.5 ns in the micelle has been determined by use of a fluorescence anisotropy analysis of Sal[−].² Because the intensity of a dielectric relaxation mode due to molecular motion is

proportional to the number of ionic pairs in the system, the proportionality of intensity for the fastest relaxation mode as seen in Figure 2 is reasonable.

However, the fact that the overall ω dependence of the dielectric spectra is independent of C_D is surprising in some aspects. It is well-known that the average contour length (l_e) between two entanglements of a threadlike material is essentially proportional to the reciprocal concentration of the threadlike material,^{12,13} i.e., $l_e \propto C_D^{-1}$ in this case. Rheological features of an entangling threadlike material are sensitive to l_e (or C_D). For example, the longest relaxation time of bending motion between entanglements in polymer solutions is proportional to the reciprocal of polymer concentration squared.¹² If the bending motion of a threadlike micelle is a distinct origin for the dielectric relaxation of the threadlike micelle in the low ω side, the longest relaxation time should strongly depend on C_D , and then, dielectric spectra cannot be superposed upon one another as seen in Figure 2. Practically, a mechanical or rheological relaxation time for the slowest bending motion between entanglements is estimated to be longer than 100 μs even at $C_D = 100$ mM. This value is much longer than the dielectric relaxation time obtained in the present study.

This argument implies that the origin of slow dielectric relaxation is not attributable to the bending motion of a threadlike micelle between entanglements. A threadlike micelle should have induced electric dipole moments to show the slow dielectric relaxation, which are different from the dipole moment due to the ionic pair. Therefore, it is necessary that the ionic pair separates into CTA⁺ and Sal[−], and a localized distribution of electric charges appears in a micelle by the migration of separated charges along the micellar surface. Since the average span of life for the ionic pair in the micelle might be independent of l_e , the shortest time to generate the smallest dipole moment, which is estimated to be 10 ns by the model functions (eq 1) in Figure 2, should be independent of C_D .

Modeling. A threadlike micelle dielectrically relaxes much faster than any conformational changes in the CTA⁺:NaSal[−]/W system. Here, we propose a model to explain the dielectric relaxation in the ω range around 10^{-7} s^{−1}. We assume the localized distribution of separated charges (induced dipole moments) as shown schematically in Figure 4b appears at kinks of a bending threadlike micelle depending on an applied electric field, which manages the dielectric relaxation in the low ω side. Furthermore, we assume the amount (q) of localized electric charges at each kink is identical. In Figure 4b, we depict three kinds of threadlike materials with different snapshots of their conformations, which have, each other, the identical l_e value and also the identical spatial distance (R_e) between entanglement points described as pinned-down points. Then, the total value (μ_{total}) of induced dipole moments for each conformation with the same l_e is approximately calculated by eq 2

$$\mu_{\text{total}} = \frac{1}{2} q \cos \theta \sum_{i=1}^n l_i = \frac{1}{2} q l_e \cos \theta \quad (2)$$

where l_i and θ are the length of a micellar contour between two opposite charges and the angle between the micellar contour and the direction of an electric field, respectively. For all the conformations in Figure 4b, $\mu_{\text{total}} = (1/2) q(l_e^2 - R_e^2)^{1/2}$ is obtained. A real distribution of the R_e^2 value and an angle (Φ) between the direction of the R_e vector and the electric field must be statistical, even if each micelle has the identical l_e value. However, the discussion above always holds in each case with any R_e^2 and Φ values. Moreover, according to the polymer chain

statistics for flexible chains,^{13,14} l_e^2 is proportional to the square (N_e^2) of the number of segments forming a threadlike material between entanglements, while R_e^2 is proportional to N_e in the unperturbed state. Therefore, the relationship of $l_e \gg R_e$ always holds for fully entangling threadlike materials with large N_e as in the CTAB:NaSal/W system. Then, the relationship of $\mu_{\text{total}} \approx (1/2)ql_e \propto C_D^{-1}$ is obtained approximately. This means that the dielectric relaxation strength of a threadlike material with the identical l_e (or C_D) value is independent of the conformation of the material. If this type of induced dipole moment appears in a threadlike micellar system, the dielectric relaxation strength is proportional to C_D . The number of threadlike micelles between entanglements is proportional to C_D^2 .

The next point is the time necessary to induce the dipole moment. If separated ions have to migrate a long distance along the contour of the threadlike micelle to make the dipole moment, the induction time for the dipole moment should depend on l_e . However, if the separation of the ionic pair propagates to a slightly separated ionic pair by exchanging a partner as depicted in Figure 4c, the ions do not have to migrate a long distance along the micelle. They only move by a distance identical to the average separation between ionic pairs to make an induced dipole moment. Thus, an induction time to make a dipole, which corresponds to the dielectric relaxation time, is essentially governed by the time necessary for the charge separation to propagate and is independent of l_e (or C_D).

An essential reason for the broad dielectric relaxation might be that rates of the propagation for charge separation along the direction of a long micellar axis and that along a direction which is perpendicular to the long micellar axis are not identical to each other. At present, further discussion on the mechanism of the slow dielectric relaxation in a threadlike micellar system is impossible. However, findings in this study will be the key to solving complicated electric birefringence phenomena observed often in the threadlike micellar systems.^{2,15} The driving force to stretch an electrically neutral threadlike micelle, such as that existing in the CTAB:NaSal/W system, into a direction along an applied electric field is directly related to the magnitude and induction time of induced electric dipole moments in the threadlike micelle.

Oizumi et al. reported dielectric behavior of an aqueous threadlike micellar system of CTAB:NaSal/W.¹⁶ Because the dielectric spectra shown in their paper hardly agreed with those we carefully determined in Figure 2, especially in the ω range

around 10^7 s^{-1} . The reason for this discrepancy should be their data-handling procedure in the lower ω side. They interpreted the dielectric dispersion around 10^8 s^{-1} on the basis of the idea of the fluctuation of electrically bound Sal^- ions in the direction perpendicular to the micellar axis.

Angelico et al.¹⁷ and Cirkel et al.¹⁸ recently reported the dielectric behavior of inverse lecithin threadlike or wormlike micelles with a water pool formed in an oil phase. They found two broad types of relaxation modes in the micellar system. A fast relaxation mode was attributed to the rotational motion of the lecithin headgroup and a slower mode to the polymer-like motion of the inverse threadlike micelle. Their interpretation of the fast mode is essentially the same as ours. However, the structure of the inverse micelles with a water pool is not clear, and there should be a number of different characteristics from a threadlike micelle formed in an aqueous media. Thus, one must be very careful when one compares the dielectric behavior of threadlike micelles formed in an aqueous environment and that of inverse threadlike micelles with a water pool formed in an oil phase.

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