Linear Viscoelastic Behavior of Perfluorooctyl Sulfonate Micelles Stabilized with Tetraethylammonium and Tetramethylammonium Cations

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For a series of aqueous solutions of perfluorooctyl sulfonate (C\textsubscript{8}F\textsubscript{17}SO\textsubscript{3}⁻; abbreviated as FOS) micelles having a mixture of tetraethylammonium (N\textsubscript{4}(C\textsubscript{2}H\textsubscript{5})\textsubscript{4}; TEA) and tetramethylammonium (N\textsubscript{4}(CH\textsubscript{3})\textsubscript{4}; TMA) ions as the counter cations, linear viscoelastic behavior was examined at 20°C. The solutions had the same FOS concentration (0.045 mol L\textsuperscript{−1}) and various TEA fraction in the counter cations, φ\textsubscript{TEA} = 0−1, and the spherical FOS micelles therein were connected into threads and further organized into dendritic networks. For φ\textsubscript{TEA} ≥ 0.5, the FOS threads/networks exhibited the Maxwell-type terminal relaxation reflecting their thermal scission. In this range of φ\textsubscript{TEA}, the terminal relaxation time τ increased with decreasing φ\textsubscript{TEA} while the steady state compliance J\textsubscript{e} was insensitive to φ\textsubscript{TEA}. On a further decrease of φ\textsubscript{TEA} below 0.3, τ became insensitive to φ\textsubscript{TEA} and J\textsubscript{e} gradually increased possibly because the motion of the threads in the unscissored form became faster than the thermal scission to govern the terminal relaxation. These rheological features were discussed in relation to the effects of TEA and TMA on the thermal scission of the FOS threads/networks: Since the charge was the same for TMA and TEA but the bare radius was smaller for TMA, the TMA cations should be preferentially bound on the FOS thread. The thermal scission of the FOS thread, occurring through an exchange of the bound and non-bound TEA cations (Watanabe et al., Rheol Acta, 28, 110 (2000)), appeared to be strongly suppressed by the preferentially bound TMA cations that effectively blocked the exchanging sites. Indeed, in a range of φ\textsubscript{TEA} ≥ 0.5 where the thermal scission governed the relaxation of the system, the rheological data were well described by a simple model considering this blocking effect.

Key Words: Perfluorooctyl sulfonate threadlike micelles / Tetraethylammonium and tetramethylammonium cations / Thermal scission / Scission catalyst / Thread motion

1. INTRODUCTION

In aqueous solutions, amphiphilic surfactant molecules form aggregates of various shapes according to their chemical structure, concentration, and temperature.\textsuperscript{1–6} Among these aggregates, threadlike micelles exhibiting prominent viscoelasticity have been subjected to extensive rheological studies.\textsuperscript{7–15}

The stress of the threadlike micelles is related to their orientation/stretching, as in the case of unbreakable polymer chains. However, these threads can be reversibly scissored and reformed due to the thermal motion of unimers (either individual surfactant molecules or their spherical micelles), and the stress relaxation occurs through this thermal scission if the scission is faster than the global motion of the threads in the unscissored form. This scission-induced relaxation is different, in some aspects, from the relaxation of the unbreakable polymer chains. For example, the thermal scission results in the Maxwell-like terminal relaxation (with the mode distribution being much narrower than that for the polymer chains), as noted for threads of 1:1 complex of cetyltrimethylammonium bromide (CTAB) and sodium salicylate (NaSal)\textsuperscript{11} and for the threads of cetylpyridinium chloride (CPyCl) and NaSal\textsuperscript{9,10,15}.

These CTAB:NaSal and CPyCl:NaSal threads have a cylindrical shape. A different type of threads is formed in aqueous solutions of tetraethylammonium (TEA) perfluorooctyl sulfonate (FOS): For these solutions, cryogenic transmission electron microscopy (cryo-TEM) revealed that the FOS molecules aggregate into spherical micelles (with the fluorooctyl groups inside) and these micelles associate with each other to form pearl-necklace shaped threads.\textsuperscript{5,6,16,17} These FOS threads, further organized into dendritic networks, exhibit the Maxwell-type terminal relaxation in the linear viscoelastic regime.\textsuperscript{16,17} This linear relaxation behavior, being attributed to the thermal scission of the FOS threads, is qualitatively similar to that of the CTAB:NaSal threads,\textsuperscript{11,12} although the

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nonlinearities under large strain/fast flow are much larger for the FOS threads because of their feebleness (due to the necked portion).\textsuperscript{16}

In attempt to clarify the thermal scission mechanism of the FOS threads, detailed NMR\textsuperscript{18,19} and rheological\textsuperscript{17} studies were conducted for the pure FOSTEA solutions as well as for binary solutions of FOSTEA and lithium perfluorooctyl sulfonate (FOSLi). The NMR studies\textsuperscript{18,19} revealed that a fraction of the TEA cations in the FOSTEA solutions is bound on the spherical FOS micelles and that the non-binding Li cations\textsuperscript{6} in the FOSTEA/FOSLi solutions enhance preferential binding of the coexisting TEA cations on the FOS micelles. These bound TEA cations, partly neutralizing the negative FOS charges, electrostatically as well as hydrophobically stabilize the FOS thread structure.\textsuperscript{18,19} Furthermore, the rheological study\textsuperscript{17} indicated that the Maxwell-type terminal relaxation time \( \tau (= \text{thermal scission time}) \) of the FOS threads having the surface saturated with the bound TEA cations is uniquely determined by a concentration of the coexisting, non-bound TEA cations, \( C_{\text{TEA}*} \)\textsuperscript{4}. Specifically, \( \tau \) was found to be proportional to \( \{C_{\text{TEA}*}\}^{-4} \). These results strongly suggest that non-bound TEA cations catalyze the thermal scission of the FOS thread through their exchange with the bound TEA cations.

In the above FOSTEA/FOSLi binary solutions, the mixing of the non-binding Li and binding TEA cations mainly results in a decrease of \( C_{\text{TEA}*} \). We expect a difference in the rheological behavior when the TEA cation is mixed with a more strongly binding organic cation (instead of Li). As a candidate of such strongly binding cations, we can choose tetramethylammonium (TMA) cation that is smaller than the TEA cation but has the same charge.

Thus, we have examined the linear viscoelastic behavior of binary FOSTEA/FOSTMA aqueous solutions having a constant FOS concentration \( C_{\text{FOS}} (= C_{\text{TEA}} + C_{\text{TMA}}) \) and various TEA mole fraction \( \phi_{\text{TEA}} \) in the cations. This paper presents the results, with an emphasis being placed on effects of the preferential binding of the TMA cations on the viscoelastic behavior.

2. EXPERIMENTAL

Tetraethylammonium (\( \text{N}(\text{C}_2\text{H}_5)_4; \text{TEA} \)) perfluorooctyl sulfonate (\( \text{C}_8\text{F}_{17}\text{SO}_3^-; \text{FOS} \)) was purchased from Aldrich and used without further purification. Tetramethylammonium (\( \text{N}(\text{CH}_3)_4; \text{TMA} \)) perfluorooctyl sulfonate was synthesized by titration of \( \text{C}_8\text{F}_{17}\text{SO}_3\text{H} \) (Fluka) with \( \text{N}(\text{CH}_3)_4\text{Cl} \) (Nacalai). After the titration in an aqueous solution, water was allowed to evaporate and the product was purified \textit{via} repeated recrystallization in dioxane, rinse with diethyl ether (to thoroughly remove dioxane), and vacuum-drying (to remove ether). The purity of FOSTMA thus obtained was confirmed from elemental analysis and NMR measurements.

The systems subjected to viscoelastic measurements were a series of aqueous solutions of FOSTEA/FOSTMA mixtures. In these solutions, the FOS concentration and the total cation concentration were the same, \( C_{\text{FOS}} = C_{\text{TEA}} + C_{\text{TMA}} = 0.045 \text{ mol L}^-1 \), and the TEA mole fraction \( \phi_{\text{TEA}} \) in the cations was varied from 0 (pure FOSTMA) to 1 (pure FOSTEA). For the FOSTEA solution, cryo-TEM confirmed that spherical FOS micelles were connected into threads and further organized into dendritic networks. The bare radius of the spherical FOS micelles (not including the TEA radius), was \( r_{\text{FOS}} \approx 1.6 \text{ nm},\textsuperscript{16} \) and each micelle is composed of \( \pm 16 \) FOS units.\textsuperscript{6} This \( r_{\text{FOS}} \) value was close to that estimated from the packing structure of the perfluorooctyl groups in the micelle, and \( r_{\text{FOS}} \) hardly changed in the presence of other cations (Li).\textsuperscript{6} Thus, the spherical FOS micelles in our FOSTEA/FOSTMA solutions should be similar, in size and structure, to those in the pure FOSTEA solutions.

Linear viscoelastic measurements were carried out with a laboratory rheometer (SR-5000, Rheometrics). A parallel-plate fixture of a diameter of 2.5 cm was used. The measurements were conducted for the FOSTEA/FOSTMA solutions at 20°C.

3. RESULTS AND DISCUSSION

3.1 Overview

For the FOSTEA/FOSTMA binary solutions having the same \( C_{\text{FOS}} (= 0.045 \text{ mol L}^-1) \) and different TEA mole fractions \( \phi_{\text{TEA}} = C_{\text{TEA}}/(C_{\text{TEA}} + C_{\text{TMA}}) \), the linear viscoelastic behavior at 20°C drastically changed with \( \phi_{\text{TEA}} \). To demonstrate these changes, Fig.1 shows the angular frequency \( (\omega) \) dependence of the storage and loss moduli, \( G' \) (unfilled circles) and \( G'' \) (filled circles), of representative solutions. In Fig.2, the terminal relaxation time \( \tau (= [G'/\omega G'']_{\omega \to \infty}) \), the zero-shear viscosity \( \eta_0 (= [G/\omega]_{\omega \to 0}) \), and the steady state compliance \( J_s (= 1/\eta_0) \) of all solutions examined are plotted against \( \phi_{\text{TEA}} \) (circles).

If the terminal relaxation is dominated by the thermal scission of the FOS threads/networks, the \( G' \) and \( G'' \) data at low \( \omega \) are described by the Maxwell model\textsuperscript{9,11,15,16}

\[
G'(\omega) = G_M \frac{\omega^2 \tau_M^2}{1 + \omega^2 \tau_M^2}, \quad G''(\omega) = G_M' \frac{\omega \tau_M}{1 + \omega^2 \tau_M^2}
\]  

(1)
Here, $G_M$ is the plateau modulus, and $\tau_M$ is the Maxwell relaxation time. We attempted to fit the $G'$ and $G''$ data with Eq. (1) to examine if the thermal scission dominates the relaxation of the FOSTEA/FOSTMA solutions. The results of the fitting are shown in Fig. 1 with the solid and dotted curves.

In Figs. 1 and 2, we clearly note that the behavior of the solutions is different for $\phi_{\text{TEA}} \geq 0.5$ and $\phi_{\text{TEA}} < 0.3$. In the pure FOSTEA solution ($\phi_{\text{TEA}} = 1$), the terminal relaxation is excellently described by the Maxwell model (cf. Fig. 1d) and thus dominated by the thermal scission of the dendritic networks of the FOS threads, as noted also in the previous study.\textsuperscript{16,17} In a range of $\phi_{\text{TEA}}$ between 1 and 0.5, the $G'$ and $G''$ data at low $\omega$ are equally well described by the model and the plateau modulus hardly changes with $\phi_{\text{TEA}}$ (cf. Fig. 1c). Correspondingly, the terminal relaxation intensity and mode distribution represented by the $J_e$ data are insensitive to $\phi_{\text{TEA}}$ ($\geq 0.5$); see Fig. 2b. Thus, for $0.5 \leq \phi_{\text{TEA}} \leq 1$, the FOS network of similar connectivity should be formed and the terminal relaxation is dominated by the thermal scission of this network, as suggested from the $\phi_{\text{TEA}}$-insensitivity of $J_e$ and the success of the Maxwell fitting. This scission is retarded with decreasing $\phi_{\text{TEA}}$ from 1 to 0.5, as noted from significant increases of the $\tau$ and $\eta_0$ data (Figs. 2a and 2c). This retardation effect is later discussed in relation to a simple model considering the preferential binding of the TMA cations on the FOS threads. (In Figs. 2a and 2c, the thick solid curves indicate the prediction of this model.)

![Figure 1](image1.png)

**Fig. 1** Linear viscoelastic behavior of the FOSTEA/FOSTMA binary solutions at 20°C. The FOS concentration and total cation concentration are the same for all solutions, $C_{\text{FOS}} = C_{\text{TEA}} + C_{\text{TMA}} = 0.045$ mol L\(^{-1}\). The mole fraction of TEA in the cations, $\phi_{\text{TEA}}$, is varied from 0 to 1.

![Figure 2](image2.png)

**Fig. 2** (a) Terminal relaxation time $\tau$, (b) steady state compliance $J_e$, and (c) zero-shear viscosity $\eta_0$ of the FOSTEA/FOSTMA binary solutions at 20°C. The FOS concentration and total cation concentration are the same for all solutions, $C_{\text{FOS}} = C_{\text{TEA}} + C_{\text{TMA}} = 0.045$ mol L\(^{-1}\). The mole fraction of TEA in the cations, $\phi_{\text{TEA}}$, is varied from 0 to 1. The thick solid curves indicate the predictions of a thermal scission model (Eq. (6)). For further details, see text.
The FOS threads/networks should be formed also in the solutions with \( \phi_{\text{TEA}} < 0.5 \), as judged from the pronounced viscoelasticity; cf. Figs.1 and 2. However, the Maxwell fitting becomes poorer with decreasing \( \phi_{\text{TEA}} < 0.3 \), as noted in Figs.1a and 1b. This failure of fitting suggests that the thermal scission at \( \phi_{\text{TEA}} < 0.3 \) is too slow to overwhelm the motion of the FOS threads in the unscissored form and thus the terminal relaxation occurs through this motion.

In relation to this failure of fitting, we note that \( J_e \) increases with decreasing \( \phi_{\text{TEA}} < 0.3 \) (Fig. 2b). Thus, the relaxation mode distribution broadens and the terminal relaxation intensity decreases on this decrease of \( \phi_{\text{TEA}} \), as also noted for the \( G' \) and \( G'' \) data (Figs.1a and 1b). These results suggest that the distributions of the length and branching degree of the FOS threads/networks change with \( \phi_{\text{TEA}} < 0.3 \). (These changes are viscoelastically detected because the motion of the unscissored threads governs the terminal relaxation at \( \phi_{\text{TEA}} < 0.3 \).

### 3.2 Preferential Binding of TMA and Thermal Scission Mechanism

The TMA and TEA cations have the same charge but the bare radius \( r^\circ \) is smaller for the former:

\[
\begin{align*}
 r_{\text{TMA}}^\circ & = 0.26 \text{ nm for TMA}, \\
 r_{\text{TEA}}^\circ & = 0.38 \text{ nm for TEA}
\end{align*}
\]

(These radii were calculated from the chemical bond lengths \( b \) of the constituent elements, \( b_{\text{C-C}} = 0.154 \text{ nm}, b_{\text{N-C}} = 0.147 \text{ nm}, \) and \( b_{\text{C-H}} = 0.11 \text{ nm} \).) This fact strongly suggests that the smaller TMA cations can be more concentrated on the FOS micelle surface to more strongly stabilize the FOS threads compared to the TEA cations. Thus, the TMA cations are expected to be preferentially bound on the FOS micelle surfaces in the FOSTEA/FOSTMA solutions, as schematically shown in Fig.3.

In the pure FOSTEA solution, the surface of the FOS micelles are saturated with a fraction of the existing TEA cations and the remaining, non-bound (free) TEA cations catalyze the thermal scission through their exchange with the bound TEA.\(^{17-19}\) We expect a similar situation in our FOSTEA/FOSTMA binary solutions: Namely, the TMA cations should be preferentially bound on the FOS micelles, and some TEA cations can be also bound if a vacancy is left on the micelle surface; cf. Fig.3b. For this case, the thermal scission would be efficiently catalyzed by the free TEA cations through their exchange with the bound TEA cations, and this scission would be faster than the motion of the threads in the unscissored form thereby governing the viscoelastic relaxation. On the other hand, no fast scission would occur if the FOS surface is saturated with TMA and no vacancy is available for TEA; cf. Fig.3c. For this case, the motion of the unscissored threads should dominate the terminal relaxation.

In the above molecular picture, a key quantity is a critical TMA fraction \( \phi_{\text{TMA}} \) in the cations for the surface saturation with TMA: The FOS surface is saturated with TMA and no fast scission occurs for \( \phi_{\text{TMA}} > \phi_{\text{TMA}}^* \) while for \( \phi_{\text{TMA}} < \phi_{\text{TMA}}^* \) some TEA cations are bound on the surface to allow the fast scission.

In the remaining part of this paper, we first attempt to estimate this \( \phi_{\text{TMA}}^* \). Then, we formulate a simple model for the relaxation time \( \tau \) in the FOSTEA/FOSTMA binary solutions of \( \phi_{\text{TMA}} < \phi_{\text{TMA}}^* \) by utilizing a relationship between \( \tau \) and the free TEA concentration \( C_{\text{TEA}} \) in pure FOSTEA solutions\(^\text{17}\)\( \text{17} \)\( \text{(} \tau \propto \{ C_{\text{TEA}} \}^{-4} \text{)} \).

### 3.3 Estimation of Critical TMA Fraction

For estimating the critical TMA fraction \( \phi_{\text{TMA}}^* \) for the surface saturation of the FOS micelles with TMA in the FOSTEA/FPSTMA solutions, we first focus on the surface coverage in the pure FOSTEA solutions.

Experiments\(^\text{17-19}\) indicated that the FOS surface in the FOSTEA solutions is saturated with a fraction of the TEA cations therein and this fraction \( f_b \) is close to 0.35. Thus, the number density of TEA on the FOS surface at saturation, \( \sigma_{\text{TEA}} \), is evaluated to be

\[
\sigma_{\text{TEA}} = \frac{n_{\text{FOS}} f_b}{4\pi r_{\text{FOS}}^2} \approx 0.17 \text{ nm}^{-2}
\]

Here, \( n_{\text{FOS}} \approx 16 \)\(^\text{18}\) is the number of FOS units per spherical FOS micelle, and \( r_{\text{FOS}} \approx 1.6 \text{ nm} \)\(^\text{16}\) is the bare micelle radius. This \( \sigma_{\text{TEA}} \) is significantly smaller than the number density for the closest surface packing of TEA evaluated from its bare radius (cf. Eq.(2)), \( \sigma_{\text{TEA}} = (1-Q)/\pi r_{\text{TEA}}^2 = 2.0 \text{ nm}^{-2} \) with \( Q = \)
1−\pi 2/3 being a vacancy fraction for the closest packing. This difference between \( \sigma_{\text{TEA}} \) and \( \sigma_{\text{TEA}}^* \) seems to reflect a large surface mobility and a mutual electrostatic repulsion of the TEA cations bound on the FOS surface: Highly mobile and repulsive cations should exhibit a surface packing much looser than the closest packing.

A similarly loose packing is expected for the TMA cations preferentially bound on the FOS surface in the FOSTEA/FOSTMA binary solutions. Assuming that a \( \sigma \sigma' \) ratio (= net occupancy on the FOS surface affected by the cation mobility and repulsion) is the same for TMA and TEA at the surface saturation, we may estimate the saturated number density of TMA as \( \sigma_{\text{TMA}} = \{n_{\text{TEA}}/n_{\text{TMA}} \}^2 \sigma_{\text{TEA}} \approx 0.36 \text{ nm}^{-2} \) (cf. Eqs.(2) and (3)). This \( \sigma_{\text{TMA}} \) value gives the number of TMA cations saturating the surface of one micelle, \( n_{\text{TMA},\text{sat}} = 4 \sigma_{\text{FOS}}^2 \sigma_{\text{TMA}} \approx 11.6 \), from which the critical TMA fraction \( \phi_{\text{c,TMA}} \) is estimated to be

\[
\phi_{\text{c,TMA}} = \frac{n_{\text{TMA},\text{sat}}}{n_{\text{FOS}}} \approx 0.72
\]  
(4) 

(Note that the number of the TEA and TMA cations per micelle is identical to the number of the FOS units per micelle, \( n_{\text{FOS}} \approx 16 \).)

From this estimate, we expect that the FOS surface is saturated with TMA and the motion of the unscissored FOS threads/network dominates the terminal relaxation in a range of the TEA fraction \( \phi_{\text{TEA}} \) below \( \phi_{\text{c,TMA}} \approx 0.28 \). This expectation is in harmony with the experimentally observed change from the Maxwell to non-Maxwell behavior and the weakening of the \( \phi_{\text{TEA}} \) dependence of \( \tau \) occurring on a decrease of \( \phi_{\text{TEA}} \) to 0.25 (cf. Figs.1 and 2), lending support to the estimated \( \phi_{\text{c,TMA}} \) value. Thus, we utilize this value to formulate a simple model for \( \tau \) in the binary solutions, as explained below.

### 3.4 Thermal Scission Model

The terminal relaxation in the pure FOSTEA solutions is dominated by the thermal scission of the FOS threads, and its characteristic time is described by an empirical equation,

\[
\tau = 1.93 \times 10^{-7} (C_{\text{TEA}}^*)^{-4} \text{ s}
\]  
(For FOSTEA at 20°C)  
(5) 

Here, \( C_{\text{TEA}}^* \) is the concentration (in unit of mol L\(^{-1}\)) of the free TEA cations catalyzing the scission through their exchange with the bound TEA cations.

In the FOSTEA/FOSTMA binary solutions, the spherical FOS micelles covered with both TEA and TMA cations are organized into pearl-necklace shaped threads, and the thermal scission should occur at the necked joints between these micelles. This scission would be supressed if the joints are covered with TMA and the exchanging/catalyzing sites for the free TEA cations are blocked. Thus, we may assume that the scission occurs only when both of the opposing surface areas of the connected FOS micelles in the joint are covered with TEA. This type of joint (FOS-TEA-TEA-FOS joint) would be formed with a probability being proportional to a squared surface number density of the bound TEA cations, and the scission time would be inversely proportional to this probability.

From this argument, we may rewrite Eq.(5) as

\[
\tau = 1.93 \times 10^{-7} \left( \frac{n_{\text{TEA},0}}{n_{\text{TEA}}} \right)^2 (C_{\text{TEA}}^*)^{-4} \text{ s}
\]  
(for FOSTEA/FOSTMA)  
(6) 

where \( n_{\text{TEA}} \) is the number of TEA cations bound on one micelle in the binary solutions, and \( n_{\text{TEA},0} \) \((= n_{\text{FOS}} f_b = 5.6)\) is that in the pure FOSTEA solution. (Eq.(6) reduces to Eq.(5) for \( n_{\text{TEA}} = n_{\text{TEA},0} \).)

In the binary solutions having \( C_{\text{FOS}} = C_{\text{TEA}} + C_{\text{TMA}} = 0.045 \text{ mol L}^{-1} \), the free TEA concentration \( C_{\text{TEA}}^* \) is given by \( C_{\text{TEA}} - n_{\text{TEA}}/n_{\text{micelle}} = 0.045 \phi_{\text{TEA}} - 0.00281 n_{\text{TEA}} \). Here, \( \phi_{\text{TEA}} \) is the TEA fraction in the cations, and \( n_{\text{micelle}} \) is the concentration of the FOS micelle in mol L\(^{-1}\) unit (\( n_{\text{micelle}} = C_{\text{FOS}} f_b / n_{\text{FOS}} \)). The bound TEA number \( n_{\text{TEA}} \) should be proportional to the surface area on the micelle available for TEA and can be expressed in terms of \( n_{\text{TEA},0} \), \( \phi_{\text{TEA}} \), and the critical TMA fraction \( \phi_{\text{c,TMA}} \) (Eq.(4)) as

\[
n_{\text{TEA}} = n_{\text{TEA},0} \left( 1 - \frac{\phi_{\text{TEA}}}{\phi_{\text{c,TMA}}} \right)
\]  
(7) 

(Note that the factor \( (1-\phi_{\text{TEA}})/\phi_{\text{c,TMA}} \) appearing in Eq.(7) represents a fraction of the FOS surface area occupied by the preferentially bound TMA.)

Utilizing the above expressions of \( C_{\text{TEA}}^* \) and \( n_{\text{TEA}} \) in Eq.(6), our model gives an explicit relationship between \( \tau \) and \( \phi_{\text{TEA}} \) for the FOSTEA/FOSTMA binary solutions having \( C_{\text{FOS}} = C_{\text{TEA}} + C_{\text{TMA}} = 0.045 \text{ mol L}^{-1} \),

\[
\tau = 1.93 \times 10^{-7} [1.389 \phi_{\text{TEA}} - 0.389]^2 [0.0231 \phi_{\text{TEA}} + 0.00615]^4 \text{ s}
\]  
(8) 

The second and third factors, respectively, represent the \( (n_{\text{TEA},0}/n_{\text{TEA}})^2 \) and \( \{C_{\text{TEA}}^* \}^{-4} \) factors appearing in Eq.(6). Since the \( J_c \) 

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data of these solutions with $\phi_{\text{TEA}} \geq 0.5$ are insensitive to $\phi_{\text{TEA}}$ ($J_e \approx 0.1 \text{ Pa}^{-1}$; cf. Fig. 2b), the zero-shear viscosity predicted from our model can be written as

$$n_0 = \frac{\eta_0}{L} = 1.93 \times 10^4 [1.389\phi_{\text{TEA}} - 0.389]^2 [0.0231\phi_{\text{TEA}} + 0.00615]^4 \text{ Pa s}$$

(9)

In Figs. 2a and 2c, these model predictions are indicated with the thick solid curves. Good agreement observed between the predictions and data for $\phi_{\text{TEA}} \geq 0.5$ lends support to the molecular picture underlying the model, the preferential binding of the TMA cations on the FOS thread surface and the thermal scission of the threads occurring only at the FOSTEA-TEA-FOS joints (not blocked by TMA) with the aid of the catalyzing free TEA cations. Concerning this result, we have to emphasize a difference between the FOSTEA/FOSMA solutions and the previously examined FOSTEA/FOSLi solutions. In the latter solutions, the Li cations were not bound on the FOS threads and the TEA cations were preferentially bound. Thus, the number of the bound TEA cations on the micelle surface, $n_{\text{TEA}}$, did not change with $\phi_{\text{TEA}}$ as long as these solutions contained a sufficient number of TEA cations. The thermal scission model for this case (Eq.(6) with $n_{\text{TEA}} = n_{\text{TEA,0}}$) satisfactorily described the $\tau$ data of the FOSTEA/FOSLi solutions, and the dominant effect of the mixing of TEA and Li was the reduction of the free TEA concentration $C_{\text{TEA}}$. The other effect emerges for FOSTEA/FOSTMA solutions examined in this study: The predictions of the model considering only the reduction of $C_{\text{TEA}}$ in Eq.(6) with $n_{\text{TEA}} = n_{\text{TEA,0}}$ are shown in Figs. 2a and 2c with the thick dotted curves. These predictions are significantly different from the data, demonstrating that the mixing of TEA and TMA have two equally important effects on the scission dynamics, the blocking of the scission sites (joints between FOS micelles) by the preferentially bound TMA and the reduction of the free TEA concentration as represented by the $(n_{\text{TEA,0}}/n_{\text{TEA}})^2$ and $\{C_{\text{TEA}}\}^{-4}$ factors in Eq.(6), respectively.

4. CONCLUDING REMARKS

Viscoelastic behavior was examined for the FOSTEA/FOSTMA binary solutions containing the threads of spherical FOS micelles that were further organized into dendritic networks. Non-Maxwell type behavior attributable to the motion of the unscissored FOS threads/networks was observed when the TEA mole fraction $\phi_{\text{TEA}}$ in the cations was smaller than 0.3, while the Maxwell-type behavior due to the thermal scission of the threads was found for $\phi_{\text{TEA}} > 0.3$. The cation radius is smaller for TMA than for TEA. Thus, TMA should have been preferentially bound on the FOS threads thereby stabilizing the FOS threads and suppressing the thread scission.

For the binary solutions with $\phi_{\text{TEA}} > 0.3$, a simple thermal scission model was formulated on the basis of the molecular picture that the surface of the spherical FOS micelles is preferentially covered with TMA and the scission catalyzed by the free TEA cations occurs only when both of the opposing surface areas of the connected micelles are covered with TEA (i.e., not blocked by TMA). The viscoelastic data of those solutions were well described by this model, suggesting the validity of this molecular picture.

REFERENCES