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SHORT COMMUNICATION

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Effect of organic salts on micellar growth and structure studied by rheology

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Abstract We report a rheological study on the effect of adding organic salts [sodium tosylate (NaTos) and benzoic acid potassium salt (BaPs)] on the micellar growth and structure of aqueous solutions of cethyltrimethylammonium chloride (CTAC) at a constant molar concentration ratio [salt]/[CTAC]. The rheological data show two well-defined domains of growth characterized by scaling laws for the surfactant concentration. The addition of NaTos leads to an unusual maximum in the viscosity-surfactant concentration curve. Before the maximum (domain 1), the analysis of the data (η_0, τ_R and G_0) suggests the presence of branched micelles (connections). After the maximum (domain 2), however, the exponents of the scaling laws do not reflect either the relaxation of this branched structure or that of an entangled transient network structure. A faster mechanism of relaxation, not yet elucidated governs their dynamics. The exponents of the power laws in the presence of the BaPs are found, however, to be in accordance with the theory of equilibrium polymers.

Key words Micelles – Connections – Rheology – Cethyltrimethylammonium chloride – Organic salts

Introduction

It is now well known that the addition of salt to aqueous cationic surfactant weakens electrostatic interactions and enhances micellar growth. When these interactions are highly screened (or in the case of neutral micelles), the scaling law behavior of this growth agrees with the theory of equilibrium polymers [1, 2]. A remarkable rheological feature of adding salt to aqueous surfactant solutions is the maximum shown by the viscosity versus salt concentration curve. This behavior is not unusual and is exhibited by many aqueous surfactant-salt systems [3–6]. The decrease in viscosity after this maximum has been explained by Lequeux [7]. In the theory he developed, linear chains are predicted to fuse and connect together to form a multiconnected (or branched) network. In this structure, the relaxation is controlled by the sliding of the connections along the cylindrical part of the micelles leading to a faster diffusion process which reduces the viscosity.

Among the variety of salts used to favor micellar growth, the most popular one is sodium salicylate (NaSal). This salt is known to confer interesting properties to micellar solutions, properties which are in part due to the presence of salicylate ions in the solution. In fact, in contrast with ordinary salts which dissolve in the bulk phase, salicylate ions are adsorbed at the micellar interface [8]. This leads to a higher screening of the interactions between polar head groups and results in the formation of very long aggregates.

Recently, we have been interested in the micellar growth induced by an increase in the amount of the surfactant, instead of salt, in systems where the electrostatic interactions are weakly screened but where wormlike micelles are formed. This could happen in systems where the added salt is dissolved at the micellar interface or close to it, as happens in systems which contain organic salts like NaSal. In our previous work [9], performed on a micellar system made of cethyltrimethylammonium chloride (CTAC) surfactant and NaSal in water (at the ratio [salt]/[surfactant] = 0.6), we found that the viscosity exhibits a maximum with varying surfactant concentration. This result is unusual, and the exponents of the scaling laws we reported on that system do not match the theoretical predictions for equilibrium polymers, whatever the reaction scheme considered for the kinetics of breaking and recombination.

In this work we investigate the effect of adding two other organic salts [sodium tosylate (NaTos) and benzoic acid potassium salt (BaPs)] on the rheology of the same surfactant as in the previous study (CTAC), in water, without adding a mineral salt and at a fixed molar concentration ratio [salt]/[CTAC]. These salts also have an aromatic ring and are expected to adsorb at the micellar interface as salicylate does. We focus our attention on the viscoelastic properties when increasing the surfactant concentration in order to obtain information on micellar growth and structure.

Theory

Rheology of linear entangled micelles

Equilibrium properties

Worm-like micelles are very long cylindrical aggregates with a typical persistence length of about 15–20 nm and a total length which can reach several microns, depending on the chemical conditions. They show some similarities with polymeric chains which relax by reptation, but in addition to the reptation mechanism, because of thermal fluctuations, micelles break and recombine [1]. This scission-recombination process leads to an exponential distribution of their size with a mean length $\bar{L}$, which is a function of the surfactant concentration. These two quantities have been calculated by Cates [2] using a mean-field approach and verified recently by molecular dynamic computer simulations [10]. In Cates' theory, the number density $N(L)$ of micelles of length L is given by

$$N(L) \sim \exp\left(-L/\bar{L}\right) \tag{1}$$

and the mean length $\bar{L}$ by

$$\bar{L} \sim C^{1/2} \exp(E_{\mathrm{sciss}}/2k_{\mathrm{B}}T) \ . \tag{2}$$

In this equation, E_{sciss} is the scission energy of a chain, k_{B} is the Boltzmann constant and T is the absolute temperature.

According to Safran and coworkers [11, 12] Eq. (2) applies in the absence of charge effects (case of neutral micelles or highly screened ionic micelles). In the absence of salt or at very low salt content, electrostatic interactions modify the micellar growth and lead to a higher exponent for the concentration dependence of $\bar{L}$.

Dynamic properties

In systems of entangled linear micelles, the relaxation of the stress is governed by competition between the reptation process (characterized by a reptation time τ_{rep} which is proportional to L^3) and the breaking-recombination process (characterized by the breaking time τ_{break} which is proportional to L^{-1}). When the mechanism of breaking is very fast compared to that of reptation ($\tau_{\mathrm{break}} \ll \tau_{\mathrm{rep}}$), as happens for worm-like micelles, the stress is found to relax with a single relaxation time as in a Maxwell fluid [13–15]. This relaxation time τ_{R} is found to be equal to the geometrical average between τ_{rep} and τ_{break}:

$$\tau_{\mathrm{R}} = \left(\tau_{\mathrm{rep}}\tau_{\mathrm{break}}\right)^{1/2} \ . \tag{3}$$

By taking into account the kinetics of breaking and recombination and its influence on the dynamic behavior, Turner et al. [16] have established scaling laws for the viscosity and the relaxation time with the volume fraction for three reaction schemes (end-to-end recombination, end-interchange and bond-interchange) under a different relaxation mechanism.

Rheology of connected micelles

According to Lequeux, the rheology of linear micelles applies for branched (or connected) chains if in some results we replace the average length $\bar{L}$ by a new length $\bar{L}_{\mathrm{C}}$ defined by

$$\bar{L}_{\mathrm{C}} = l_{\mathrm{p}} n_2/(n_1 + 2n_3) \ . \tag{4}$$

In this equation n_1 corresponds to the concentration of end caps or extremities, n_2 designates the density of the persistence length, n_3 the concentration of the connections and l_{p} the persistence length. Depending on the relative dominance of the connections or the extremities, two limits can be drawn:

1. If no connections are present ($n_3 = 0$), $\bar{L}_{\mathrm{C}}$ scales as $\bar{L} \sim C^{1/2}$.
2. If the structure is completely connected ($n_1 = 0$), $\bar{L}_{\mathrm{C}}$ scales as $C^{-1/2}$.

The presence of connections does not affect the viscoelastic behavior which still shows a Maxwell behavior, but the quantity G''_{min}/G_0 scales with a different exponent of the surfactant concentration. This exponent becomes −3/4 when connections are present in the system instead of −7/4 in the absence of connections. The minimum of $G''(\omega)$, which is related to the entanglement length and to $\bar{L}_C$ (or to $\bar{L}$ when no connections are present), is given by

$$G''_{\min}/G_0 \sim L_\epsilon/\bar{L}_C \sim C^{-7/4}, \tag{5}$$

with

$$G_0 \sim C^{2\text{–}2.3}. \tag{6}$$

Materials and methods

Samples

The solutions studied in this work are made of the surfactant CTAC and one of the two organic salts NATos and BaPs in water. These salts also have an aromatic ring and are expected to adsorb at the micellar surface. Especially, the tosylate salt is known to favor micellar growth by acting as a cosurfactant like NaSal [17]. As in the previous study, the ratio [salt]/[CATC] is kept constant.

Rheological measurements

The rheological measurements of the samples made with NaTos were carried out using a controlled stress rheometer (Carrimed CSL 100) at a constant temperature of 30 °C. We used a cone-plate geometry with an angle of 30′ and a gap of 13 μm. Because of the fluidity of the solutions made with BaPs, the viscosity measurements were performed with a capillary viscometer (Ubbelohde tube).

Frequency sweep measurements were performed at a given stress σ_0 (chosen in the linear domain where the amplitude of the deformations is very low) in the frequency (ω) region varying from 0.01 to 100 rad/s.

To determine the elastic modulus G_0 and the relaxation time τ_R, we used the data of the storage modulus G' and the loss modulus G'' as a function of the frequency.

In the case of a Maxwell fluid, $G'(\omega)$ and $G''(\omega)$ are given by the following equations:

$$G'(\omega) = G_0\omega^2\tau_R^2/(1+\omega^2\tau_R^2) \tag{7a}$$

$$G''(\omega) = G_0\omega\tau_R/(1+\omega^2\tau_R^2), \tag{7b}$$

with

$$\eta_0 = G_0\tau_R. \tag{8}$$

Here η_0 is the zero-shear-rate viscosity, G_0 is measured at high frequency where G' reaches a plateau and τ_R is equal to the inverse of the frequency ω (rad/s) at which G' is equal to G''. Also of interest is a linear plot of G'' versus G' which reveals the semicircle (Cole–Cole) characteristic of a Maxwell fluid.

Results

System CTAC + NaTos + water

We first measured the zero-shear viscosity of a 0.1 M/l CTAC sample as a function of the salt concentration, which we varied between 0.06 and 0.18 M/l. These results are reported in Fig. 1. The viscosity shows first a sharp increase at low salt concentration until a maximum of 30 Pa.s at 0.08 M/l and then decreases: this behavior is expected. It is similar to the behavior obtained in several aqueous surfactant/salt systems and is explained by connections which result from the fusion of the micelles.

We then studied this system at a fixed concentration ratio [NaTos]/[CTAC] of 0.8 (ratio corresponding to the maximum of the viscosity) at 30 °C. The evolution of the viscosity as we varied the surfactant concentration is plotted in a log-log plot in Fig. 2. This behavior is similar to that of the CTAC/NaSal system [9]. This curve shows a maximum of 350 Pa.s at a surfactant concentration of 0.45 M/l. This maximum separates two well-defined domains showing a characteristic scaling behavior for the surfactant concentration. In the first domain, the viscosity increases with a power law with an exponent of 2.1. Here again, even if this exponent is twice that obtained for the CTAC/NaSal system, it is still lower than all the theoretical values predicted for all reaction schemes considered in Ref. [16]. Above this maximum, in domain 2, a less-pronounced decrease in

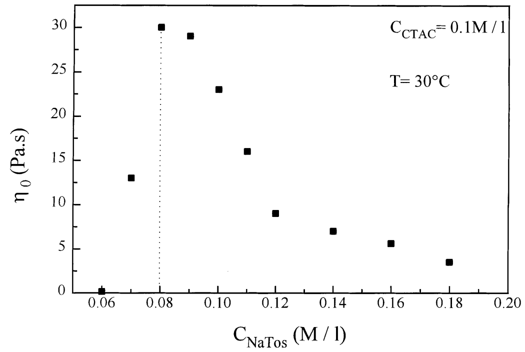

Fig. 1 Zero-shear viscosity η_0 of a 0.1 M/l cethyltrimethylammonium chloride (*CTAC*) solution as a function of sodium tosylate (*NaTos*) concentration at 30 °C

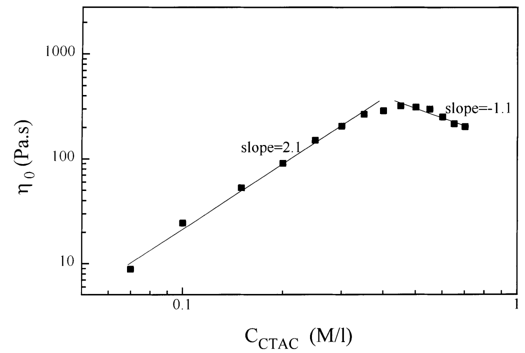

Fig. 2 Zero-shear viscosity η_0 as a function of surfactant concentration with the ratio [NaTos]/[CTAC] = 0.8 at 30 °C

viscosity (than with NaSal) is obtained with an exponent of −1.1.

The Cole–Cole plots obtained from frequency measurements for all the concentrations studied are reported in Fig. 3. These plots have a semicircular shape for concentrations lower than 0.55 M/l CTAC. Above this concentration the shapes of the curves are altered and show some deviations from semicircles at high frequencies.

The evolution of the relaxation time deduced from these measurements is reported in Fig. 4. These data also show a break in slope at a maximum which occurs at the same surfactant concentration as for the viscosity data. The relaxation time τ_R increases in domain 1 with an exponent of 0.22 and then decreases following a power-law behavior with an exponent of −2 at high concentrations. The relaxation after the maximum becomes faster as the system becomes more concentrated. This behavior is the opposite of what is usually observed for worm-like micelles.

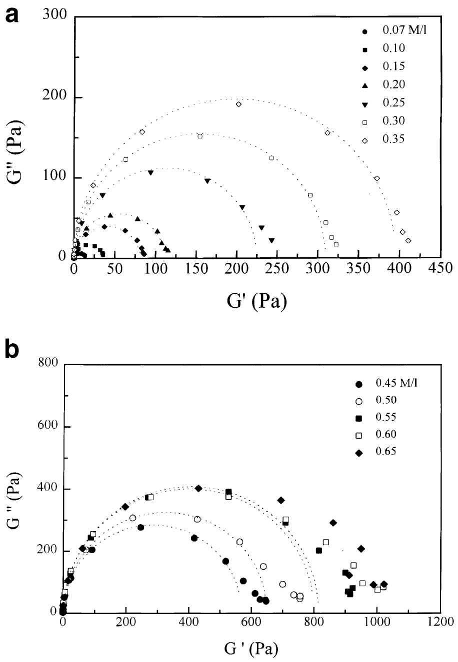

Fig. 3a Cole–Cole plots of different surfactant concentrations varying from 0.07 to 0.35 M/l with the ratio [NaTos]/[CTAC] = 0.8 at 30 °C. **b** Cole–Cole plots of different surfactant concentrations varying from 0.45 to 0.65 M/l with the ratio [NaTos]/[CTAC] = 0.8 at 30 °C

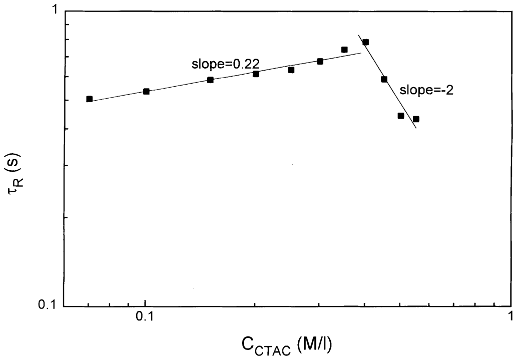

Fig. 4 Relaxation time τ_R as a function of surfactant concentration with the ratio [NaTos]/[CTAC] = 0.8 at 30 °C

The elastic modulus plotted against the CTAC concentration is given in Fig. 5. This curve does not show any discontinuity and G_0 follows a monotonous evolution and shows the same scaling law with an exponent of 1.9 in the entire concentration domain explored. This exponent is very close to the one we obtained in our previous work (1.7 for the CTAC/NaSal system) but is low compared to the theoretical value, which is predicted to range between 2 and 2.3.

Experimental values for the exponent of the viscosity with C as low as the one we find in this work and in the previous study have been reported in the literature [18]. A value of 1.3 for the exponent of the viscosity and an exponent of −1 for the relaxation time (very close to what we found for the previous system, 1.1 and −0.76 for η_0 and τ_R, respectively) have been reported by Hoffmann [18] in a study of the CPyCl system. To explain the ϕ^{-1} dependence of the relaxation time Hoffmann allowed for the possibility for micelles to connect or to fuse together and pointed out that systems which show such low exponents are close to the L_1/L_α boundary.

System CTAC + BaPs + water

The variation of the zero-shear-rate viscosity with the salt concentration of a 0.2 M/l CTAC concentration is reported in Fig. 6. The viscosity of this system is much lower than those obtained with NaTos and NaSal but it follows the same evolution; that is, η_0 increases first with increasing salt concentration until a concentration of 0.2 M/l and decreases after this maximum (around 3 Pa.s).

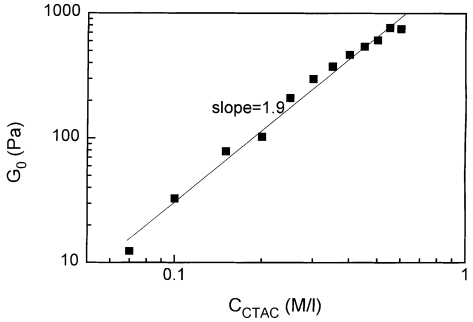

Fig. 5 Variation of the elastic modulus G_0 as a function of surfactant concentration with the ratio [NaTos]/[CTAC] = 0.8 at 30 °C

At a fixed concentration ratio of 1 (corresponding to the maximum of the plot in Fig. 6), the viscosity increases with surfactant concentration in the whole concentration domain explored, between 0.1 and 0.7 M/l (Fig. 7), in contrast with the previous system. However, the evolution of η_0 is not monotonous. It shows a break, and its slope becomes less steep than in the first domain. Here again, two domains can be distinguished and characterized by two power laws with different exponents. In the first one, below a concentration of 0.25 M/l, growth is strong with a power of 4.9. This value is close to the one (5.7) predicted for systems of unbreakable chains. This is the case when micelles are short and consequently have very long breaking times. This salt seems to be less efficient than NaTos or NaSal in favoring micellar growth, as can be seen in the values of the viscosity, which are very low compared to the system which contains the tosylate salt. The maximum of the viscosity is 100 times lower that with NaTos even if the surfactant concentration is 2 times higher in the system with BaPs.

In domain 2, the growth is less pronounced with an exponent of 2.4. This exponent is comparable to the theoretical value (2.9) predicted for systems where Rouse modes by "breathing" dominate the relaxation and where the kinetics of breaking recombination is controlled by the exchange of extremities (end-to-end recombination). Rouse effects can be seen in the Cole–Cole plots of Fig. 8, which show deviations from a perfect circle at high frequencies: deviations are a sign of these effects.

For low surfactant concentrations (under 0.2 M/l), the limits of our apparatus do not allow higher frequency measurements.

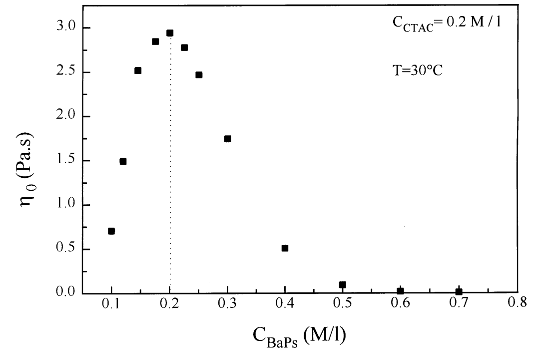

Fig. 6 Zero-shear viscosity η_0 of a 0.2 M/l CTAC solution as a function of benzoic acid potassium salt (*BaPs*) concentration with the ratio [BaPs]/[CTAC] = 1 at 30 °C

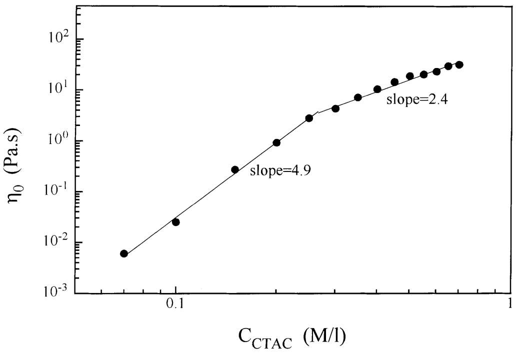

Fig. 7 Zero-shear viscosity η_0 as a function of surfactant concentration with the ratio [BaPs]/[CTAC] = 1 at 30 °C

Conclusion

BaPs acts weakly on micellar growth as indicated by the low values of the viscosity. Compared to NaTos, this salt does not seem to be strongly bound to the micellar interface. At low surfactant concentration (domain 1), the micelles are short (with a long breaking time), and the breaking-recombination process does not affect the dynamic behavior. As a result, relaxation occurs as in systems of unbreakable chains, controlled by pure reptation. In the second growth domain, the breaking-recombination process, which arises through an end-to-end recombination mechanism, becomes more influential and affects the relaxation.

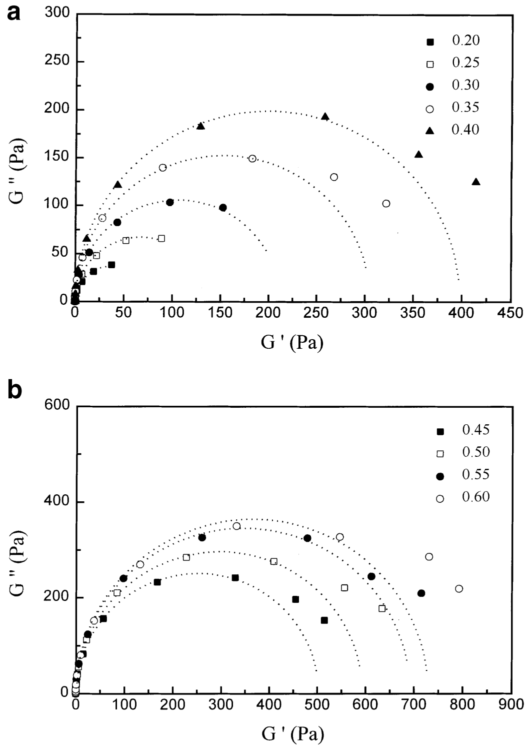

Fig. 8a Cole–Cole plots of different surfactant concentrations varying from 0.2 to 0.4 M/l with the ratio [BaPs]/[CTAC] = 1 at 30 °C. **b** Cole–Cole plots of different surfactant concentrations varying from 0.45 to 0.60 M/l with the ratio [BaPs]/[CTAC] = 1 at 30 °C

When adding the NaTos salt, the exponents of the scaling laws shown by the viscosity and the relaxation time in the first domain are very low compared to the theoretical ones. Analysis of the data suggests the development of connections which lead to a small increase in viscosity. The idea of the existence of these connections is reinforced by the value of the exponent of the elastic modulus (1.9), which does not match the theory of classical networks. Because of sliding, the connections should contribute less to the elasticity than the entanglements do. This explains the modest increase of the elastic modulus with surfactant concentration.

The variation of the quantity G''_{min}/G_0 as a function of the surfactant concentration for the systems with NaTos and NaSal (from the data of the previous work) is shown in Fig. 9. We were not able to do these calculations with BaPs as this salt does not allow the determination of G_0. This ratio goes through a minimum which corresponds to the maximum of the viscosity and to the change in the slope of the relaxation-time curve. The exponents of the scaling law in the first domain, -0.9 and -1 for NaTos and NaSal, respectively (which are practically equal), are between the limits $-7/4$ (absence of connections) and $-3/4$ (saturated connections). According to the model of Lequeux, these exponents are also in agreement with the presence of connections in this concentration domain.

In domain 2, the exponents of the scaling laws for η_0 and τ_R are unusual. At the present time there is no theory which predicts or explains this scaling or these negative exponents for the surfactant concentration. The strong decrease of the relaxation time in domain 2 suggests a decrease in the micellar length. However, this possibility should be dismissed since the elastic modulus follows a monotonous increase, which indicates that the same structure exists in the two domains. The behavior of the viscosity with changing concentration is the result of the change in the relaxation time instead of a structural change. This monotonous increase of the elastic modulus also eliminates the possibility of the boundary of the Onsager regime, otherwise G_0 should decrease.

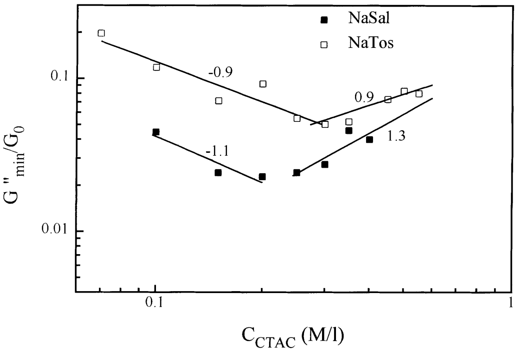

Fig. 9 Variation of G''_{min}/G_0 as a function of surfactant concentration for [*NaSal*]/[CTAC] = 0.6 and [NaTos]/[CTAC] = 0.8 at 30 °C

When viewing the samples between crossed polarizers the samples do not show any birefringence at rest. There is no evidence of the formation of a liquid crystalline phase.

The mechanism which governs the relaxation in the second domain is still unknown and more work needs to be done to elucidate the relaxation behavior.

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