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Onion-Like Structure of Viscoelastic Surfactant Solution Flow Induced by 4-Blade Paddle Impeller in a Vessel

Yoshiyuki Komoda, Kazuhiro Kobayashi and Hiroshi Suzuki

Department of Chemical Science and Engineering, Kobe University, 1-1 Rokkodai-cho, Nada-ku, Kobe-shi, Hyogo 657-8501, Japan

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Aqueous solutions of some kinds of surfactants and counterions are known as viscoelastic fluids. The rheological properties and fluidity of the solutions are significantly affected by the surfactant and counterion concentrations. Thus, the solution is a potential solvent for industrial applications because a drastic change in the fluidity can be realized only through the addition of counterions. In this study, we focused on the characteristics of the fluid flow of viscoelastic surfactant solutions in a mixing vessel. It was found that in the vicinity of the impeller the fluid was actively mixed and contained a large number of laminated fluid lumps, forming onion-like structure. When the elastic force becomes comparable to the viscous force, the micellar network of the surfactant was deformed. Additionally, if the elastic force was not much smaller than the inertia force, the impeller region was covered by a network-deformed fluid and an onion-like structure was then formed. Moreover, a stable onion-like structure was obtained when the impeller rotated as slowly as possible or when the elastic force of the solution was more significant than the viscous one.

Introduction

It is well known that surfactant molecules in water aggregate to form micelles with various shapes above a critical micellar concentration. It has been reported that ionic surfactant molecules can form rod-like micelles with the aid of counterion because electrical charges of the surfactant head group are neutralized by counter-charged ions. The rod-like micelles form an entangled structure as well as many linear polymer chains, and the surfactant solution shows significant viscoelasticity (Clausen *et al.*, 1992). Some kinds of rod-like micelles or linear polymers are known to deform and form bundled structures in a simple shear flow, for example, in flows near plates. The bundled structure plays a role in restricting the transportation of turbulence in the flow, and the fluid flow then remains in the laminar regime even at large flow rates. This is the well-known drag-reducing effect. The mechanism and efficiency of drag reduction have been intensively studied (Rose and Foster, 1989; Hu and Matthys, 1995; Myska and Zakin 1997; Lu *et al.*, 1998; Lin *et al.*, 2001; Usui *et al.*, 2004; Suzuki *et al.*, 2005). The viscoelasticity of the surfactant solution disappears and recovers depending on the applied shear rate and shearing time because the entangled micellar structure or rod-like micelles are destroyed in a strong shear flow and rebuilt by removing the applied shear stress, while once degraded polymer molecules are not restored (Myska and Zakin, 1997). Additionally, in contrast to the case of polymer solutions, the rheological properties of surfactant solutions can be easily controlled by the addition of surfactants or counterions without chemical reactions. That is, the fluidity in a confined vessel or flow geometry is easily and drastically changed by adding a small amount of additives.

Surfactants are widely used in industrial processes as additives. Industrial application of viscoelastic surfactant solutions are increasing. One of the trends is the use of drag-reducing solutions in reducing the energies required in agitating and pumping a fluid. The substitution of the agitating medium, which is generally water, with these solutions is helpful for developing an energy-saving mixing process (Choi *et al.*, 2000; Ge *et al.*, 2007). Measurements of velocity profiles have clarified that the drag reduction in a mixing vessel is caused by the laminarization of flow near the vessel wall even under turbulent mixing conditions (Mavros *et al.*, 2011). In contrast, fluid flow in the region near the mixing impeller will be intensive and that near the vessel wall will be moderate at a low rotational speed. It has been reported that large particles with a narrow size distribution were obtained in a crystallization process with this characteristic fluid flow (Montantea *et al.*, 2011). The cores of crystals are formed in the center region and they then grow into large crystals in the outer region. The viscoelasticity of the polymer (PAA) solution that Montantea *et al.* (2011) used is difficult to change during crystallization.

The viscoelasticity of a surfactant solution with counterion has long been studied and is known to be controlled by various factors, including the concentrations of the surfactant and counterions, ionic strength, water quality, and temperature. The mechanism of viscoelastic change has not been clarified but viscoelastic changes are presumably caused by structural changes in rod-like micelles, such as branches, bundles, saturation of entanglement (Lin *et al.*, 2001). Nevertheless, it is true that the rheological properties of a viscoelastic surfactant solution are strongly affected

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Correspondence concerning this article should be addressed to Y. Komoda (E-mail address: komoda@kobe-u.ac.jp).

by the concentration of counterions, and interestingly, the viscoelasticity does not monotonously change with an increase in the counterion concentration. We have reported that in an Ethoquard O/12 (surfactant)–sodium salicylate (counterion) system, an increase in the elasticity of the solution is followed by a decrease above a critical concentration, with increasing counterion concentration (Usui *et al.*, 2004). Thus, establishing a three-step crystallization process to induce drastic rheological changes appears to be feasible. The cores are generated in a less viscous surfactant solution without counterions, crystals are grown in a viscoelastic solution by the addition of counterions, and finally, crystals are easily separated from the less viscous surfactant solution containing an excess amount of counterions. As the first step in the development of the intensified crystallization process, we have researched the flow of a viscoelastic surfactant solution in a mixing vessel for various surfactant and counterion concentrations.

1. Experimental

1.1 Materials

The cationic surfactant and counterion supplier used in this study were oleyl-*bis*-hydroxyl-methyl-ethyl-ammonium chloride (supplied by Kao Corp.) and sodium salicylate (purchased from Wako Pure Chemical Industries, Ltd.), respectively. These materials were dissolved in deionized water, and the surfactant solutions were agitated using a magnetic stirrer for more than one day. Many of the rheological studies of viscoelastic surfactant solutions deal with highly concentrated solutions with a concentration on the order of 5 wt% because of the high accuracy of rheological measurements. In this study, since a less viscous solution without counterion is preferable, the surfactant concentrations, C_S, were considered 1000, 2000, and 4000 ppm. The concentration of the counterions was determined as molar ratio to surfactant, ξ, and it was varied from 0 to 5.

1.2 Rheological characterization

A stress-controlled rheometer (MCR-301, Anton Paar GmBH) was used to measure the viscosity, η, and first normal stress difference, N_1, of the surfactant solutions using a cone and plate geometry (the diameter and angle of the upper cone was 50 mm and 1°). In order to stabilize the micellar structure in the gap between the cone and plate for a rotational flow, a preshear at the shear rate of $1\,s^{-1}$ was first applied for 1 min. The shear rate was changed from 0.1 to $1000\,s^{-1}$, and the stable values of the shear stress and normal force exerted on the upper cone at each shear rate were used to obtain the viscosity and first normal stress difference. The viscoelasticity of surfactant solutions disappears at high temperatures because the thermal energy overcomes the energy associated with the entanglement of micelles. Thus, rheological measurements were conducted at 12°C.

1.3 Visualization of fluid flow in a mixing vessel

Surfactant solutions were agitated in a cylindrical glass vessel (inner diameter: 12 cm), that was equipped with a rectangular acrylic vessel to avoid optical distortion. The glass vessel was filled with a surfactant solution up to a liquid height of 12 cm, and a four-blade paddle impeller having a diameter and height of 7 cm and 1 cm was positioned at the center of the vessel. That is, the impeller was located at a distance of 6 cm from the bottom and was concentric to the vessel. The shaft connected to the impeller was rotated by a motor (BL300R, Shinto Scientific Co., Ltd.) at rotational speeds, N, up to 300 rpm. By circulating temperature-controlled water in the space between the inner and outer vessels, the temperature of the surfactant solution was adjusted to around 12°C.

Two kinds of light sources were used to visualize the impeller-induced fluid flow in the plane of the mixing shaft in the cylindrical vessel. Radiation from a halogen lump (KTX-100R, Kenko Co., Ltd.) was focused on the surfactant solutions through a slit (2 mm in width). If the surfactant molecules form a sufficiently large entangled network, the network scatters the light and the solution becomes cloudy. Conversely, a clear solution implies that no scattering structure exists in the vessel. Furthermore, a laser light sheet (DPSS Green Lasers, Japan Laser Corp.) and a fluorescent dye, Rhodamine B (Wako Pure Chemical Industries Co., Ltd.), were also used. A small amount of the surfactant solution containing the dye was injected at various points, and traces of the fluid could be clearly observed. The fluid flows were recorded using a high-density video camera (HDR-HC3, Sony Corp.), and all images that presented in this paper were captured from the recorded video files.

2. Results and Discussion

2.1 Rheological properties

The viscosity and normal stress difference of the surfactant solutions are shown in **Figure 1**. At $\xi=0$ and $C_S=2000$ ppm, the solution shows a constant viscosity and zero normal stress. This result indicates that surfactant molecules form spherical micelles only in the absence of the screening effect of counterions. At a sufficiently low surfactant concentration, the interaction between spherical micelles can be neglected because of large distance, and the solution behaves as a Newtonian solution. At $\xi=2$, the viscosity is roughly constant at 30 mPa·s up to the shear rate of $3\,s^{-1}$ and decreases gradually with increasing shear rate. The normal stress difference begins to increase dramatically at the shear rate of $10\,s^{-1}$. These shear-thinning and viscoelastic behaviors indicate the deformation of entangled networks of rod-like micelles. The network structure was retained at a low shear rate and the viscosity did not change despite an increase in the shear rate. The structure will be deformed with an increase in the shear rate and the solution will flow more easily, which implies a decrease in the viscosity. At a higher shear rate, the structure will be strongly deformed and tend to shrink in a direction perpendicular to the flow direction. To examine the amount of deformation, the stress normal to the rotational disk was measured. The

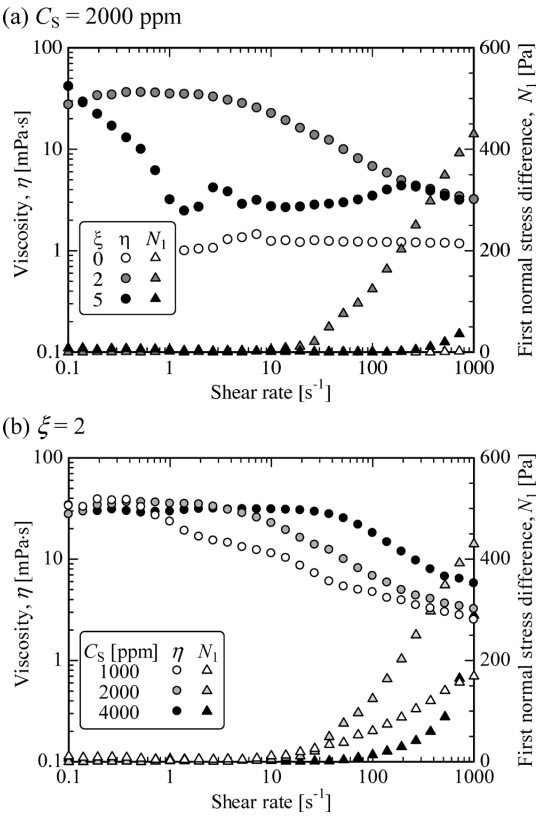

Fig. 1 Rheological property of surfactant solutions

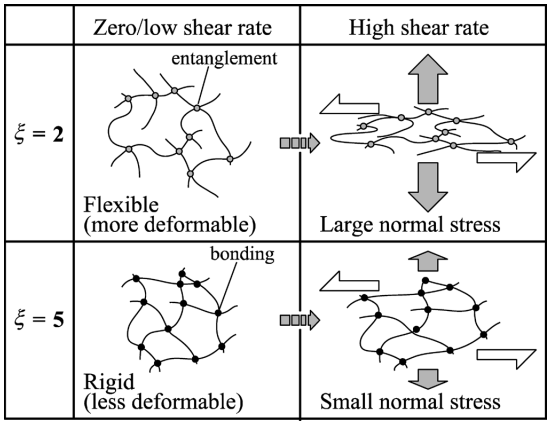

Fig. 2 Process of deformation of micellar network and normal stress development (C_S=2000 ppm)

process of deformation of micellar networks is illustrated in **Figure 2**. The solutions with ξ=5 showed a viscosity similar to that of the solution ξ=2 at the shear rate of 0.1 s^{-1}, and the viscosity dropped abruptly to 3 mPa·s at shear rates above 1 s^{-1}. Since the connecting points of micelles change from entanglement to molecular binding upon the addition of excess counterions (Lin *et al.*, 2001), bound micellar network behaves as a single rigid object. Thus, with increasing shear rate, weakly flocculated bound structures are dispersed. These are the reasons why the viscosities showed a drastic drop and smaller constant values at a low shear rate compared to ξ=2. However, the viscosities of the solution agreed well with those if the solution with ξ=2 in the higher shear rate region. The good agreement implies that similar micellar network structures were formed under high shear stress in the solutions with different concentrations of the counterions. Additionally, the solution showed a very small normal force at shear rates above 500 s^{-1}. Since the bounded micellar network is difficult to deform, no bounce-back effect was observed below this value of the shear rate, as shown in Figure 2.

The rheological characteristics of the surfactant solution were affected by the surfactant concentration as well. Figure 1(b) shows the shear rate dependence of the rheological properties of surfactant solutions with different surfactant concentrations at a constant counterion molar ratio. The viscosities at shear rates below 1 s^{-1} were constant and not affected by the surfactant concentration. For the surfactant–counterion system used in this study, it has previously been reported that for ξ=1, the zero shear viscosity increases and then decreases, while for ξ=2.5, decreases and then increases with an increase in the surfactant concentration (Lin *et al.*, 2001). For ξ=2, the constant viscosities at small shear rates are conceivable and are probably the result of a balance between the density and size of micellar networks. That is, with increasing surfactant concentration, the interaction between networks will be significant while every network becomes less flexible. In addition, when the viscosity began to decrease, the shear rate increased with the surfactant concentration. Since the viscosity decrease indicates the deformation of the networks, for decreasing viscosity, a higher shear rate at a high surfactant concentration corresponds to stiffer micellar networks. The first normal stress difference results are also interesting: the 2000 ppm solution had the largest normal force. The micelles in a 1000 ppm solution are loosely entangled. So, although the networks are easily deformed, they do not show a large normal force owing to the presence of a small number of micelles. In contrast, stiff micelle networks require a high shear rate to deform, and the normal force of the 4000 ppm solution did not exceed that of the 2000 ppm solution in the shear rate range investigated. The former solution had a larger normal stress than the latter solution at shear rates above 1000 s^{-1}.

2.2 Visualization of mixing region with slit light

When the surfactant solutions with ξ=2 and 5 were illuminated by a slit light, they became cloudy and were observed as bright parts, as shown in **Figure 3(a)**. Since the size of micelles was reported to be 330 nm (Myska *et al.*, 1997), it is clear that the clouding resulted from the scattering of light by the micellar structures. When the solution with ξ=2 was agitated above 20 rpm, it was seen that the impeller was covered by several layers of dark fluid lumps to form an onion-like structure (**Figure 3(b)**). It was also observed that the dark parts were pushed outward radially from the impeller edge four times in one revolution of 4-blad impeller and they appeared to become bright at the outer edge of the onion-like structure. Once the impeller rotation was stopped, it was observed that the dark part dis-

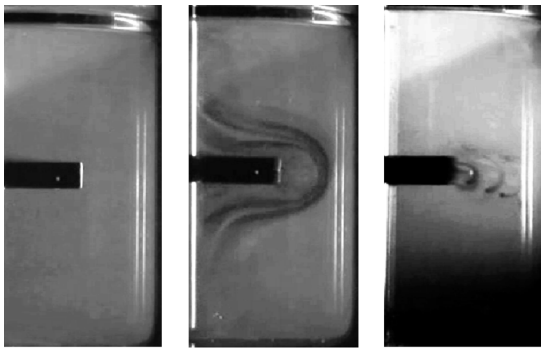

Fig. 3 Onion-like structures around the impeller: (a) $\xi=2$, $N=0$ rpm, (b) $\xi=2$, $N=50$ rpm, and (c) $\xi=5$, $N=150$ rpm. $C_S=2000$ ppm for all photos

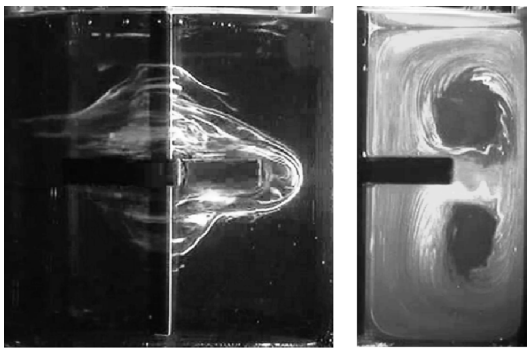

Fig. 4 Fluid flow in the mixing vessel ($N=50$ rpm). The molar ratios of counterions were (a) 2 and (b) 5 with $C_S=2000$ ppm

appeared gradually. Thus, the dark part layers in the bright bulk suggest that the application of a strong shear stress near the impeller edge would temporarily deform the micellar structure in the rotational direction and the part of the fluid not scattering light were observed to be dark.

In the solution with $\xi=5$, no onion-like structure was observed at 20 rpm, and there were dark part lumps being pushed out from the impeller at 150 rpm, as shown in Figure 3(c). The viscosity of the solution with $\xi=5$ began to decrease and N_1 began to increase over 200 s^{-1}, which is much larger than 10 s^{-1} for the $\xi=2$ solution. The viscosity decrease and the increase of N_1 indicate the deformation of entangled structure. Thus, it was concluded that the $\xi=5$ solution required a higher shear rate than the $\xi=2$ solution to change the solution from bright to dark. Although the micellar networks in the solution with $\xi=5$ might be significantly deformed at 150 rpm, the dark fluid lumps could not envelope the impeller owing to the strong discharge flow. In contrast, the solution with $\xi=0$ was transparent regardless of the rotational speed. This solution did not have any entangled structures and a structure change would not have taken place even in a strong shear flow.

If the deformed micellar network can recover before the next blade passage, the dark parts being pushed out from the impeller edge should not be observed. In other words, whether the solution will become dark can be determined from the Weissenberg number, *We*, which is the ratio of structure relaxation time to characteristic process time. The time interval between blade passages is taken as the process time, and the Weissenberg number is defined by Eq. (1) below;

$$We = n(N/60)\cdot\tau_r \tag{1}$$

where n represents the number of blades ($n=4$).

The relaxation times of the surfactant solutions of 2000 ppm are roughly predicted to 2 s ($\xi=2$) and 0.1 s ($\xi=5$) on the basis of our previous work (Watanabe *et al.*, 2008). As a result, the Weissenberg numbers at the minimum rotational speed required to generate a dark part, N_{min}, are 2.7 ($N=20$ rpm, $\xi=2$) and 1.0 ($N=150$ rpm, $\xi=5$), respectively. Since the Weissenberg number also represents the ratio of elastic force to viscous force, a dark part will be observed when the elastic force is comparable to the viscous force. It was also found that the emergence of a dark part suggests that the deformed micellar structure does not recover between blade passages.

2.3 Fluid flow and formation of onion-like structure

For the sake of visualization of the fluid flow in the whole vessel, the dye solution was injected as a tracer at several points near the impeller after achieving a stable fluid flow. The images in **Figure 4** show the difference in the fluidized region between two different molar ratios of the counterions. At $\xi=2$, the dye solution did not spread over the whole vessel and was seen to envelope the impeller. The onion-like structure observed in Figure 3(b) essentially indicates the same phenomenon as that in the case of a fluid lump spiral. The characteristic fluid flow near the impeller was similar to "cavern" that is frequently seen when a yield stress fluid is agitated (Solomon *et al.*, 1981). However, the fluid outside the onion-like structure flowed moderately because the solution had a low and constant viscosity, while the fluid outside the cavern was completely stagnant owing to the yield stress. In contrast, for $\xi=5$, the dye solution mixed with the whole fluid in a short time, and most of the fluid became colored, even though a pair of isolated mixing regions was formed above and below the impeller edge. Since the isolated mixing regions will be easily destroyed upon the installation of baffles or upon increasing the rotational speed, homogeneous mixing can be achieved for the solution with $\xi=5$.

For experimental conditions identical to those of Figure 4 (a), the fluid flows inside the onion-like structure were visualized by injecting the dye solution into two points near the shaft, as shown in **Figure 5**. Since the shaft did not penetrate the impeller in this experimental setup, we also examined the effect of the shaft on the fluid flow. Initially, the dye solution injected just above the center of the impeller move circularly with the rotating impeller; stretched in the radial direction and finally trapped in the vicinity of the impeller-sweeping region (Figure 4(a)). Thus, the fluid was actively mixed in the core of the onion-like structure and isolated from the other regions. In contrast, the dye solution injected

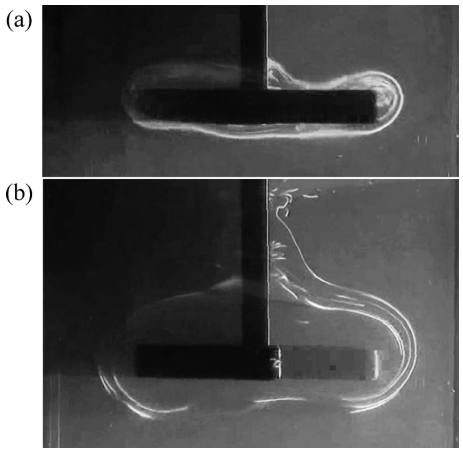

Fig. 5 Core and shell of onion-like structure: (a) Core was visualized by injecting tracer fluid near the center of the impeller, and (b) Shell was by injecting the fluid near the shaft, respectively. Test fluid of $\xi=2$ and $C_S=2000$ ppm was agitated at 50 rpm.

at the top of the onion-like structure formed a winding pattern either around the shaft because of the Weissenberg effect or in the core region because of the centrifugal force, and it then formed the shell structure over the core region (Figure 4(b)). Finally, while the onion-like structure with several layers of shells was colored by the tracer fluid, the center of the structure remained uncolored. Therefore, the core region of the structure was covered by the fluid that spiraled down the core region (dominated by the inertia force) and then by the fluid that spiraled up (dominated by the elastic force). The pattern is one of the popular flow patterns observed around a rotating sphere in a viscoelastic solution (Ulbrecht and Patterson, 1985). The fluid that spiraled down was pushed out from the impeller edge during the blade passage and again spiraled up forming shells. Thus, it was found the onion-like structure was quite different from the cavern and was composed of an isolated mixing region (core) and surface flows in opposite directions (shell). Furthermore, a dye solution injected near the vessel wall was stretched and moved circularly in the clockwise direction slowly. The rotational direction was opposite to that predicted from the discharge flow from the impeller edge and must have been caused by a secondary flow. The secondary flow of a viscoelastic fluid in a mixing vessel is well-known phenomenon (Stokes and Boger, 2000). A part of the fluid in the shell region was captured by the secondary flow and spread in the outer region of the onion-like structure. It was also found that the formation process and core-shell isolation of the onion-like structure were not affected by the asymmetry of the shaft, except for the bottom shape of the onion-like structure.

2.4 Dimensions and development of onion-like structure

The dimensions of the onion-like structure did not show drastic changes at low rotational speeds, even though the structure periodically expanded and contracted with the passage of the impeller blade through the plane illuminated

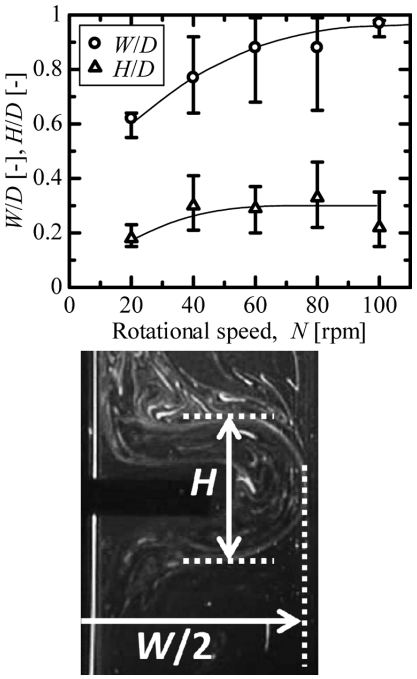

Fig. 6 Size development of onion-like structure against rotational speed of the impeller for the solution of $\xi=2$ and $C_S=2000$ ppm

by the light sheet. As the rotational speed increased, the expansion and contraction of the onion-like structure were more significant and frequent. Hence, the size changed drastically even at a constant rotational speed, and the change was out of phase with blade passage. The width and height of the onion-like structure were measured from images captured from videos and plotted against the rotational speed as ratios to the vessel diameter (**Figure 6**). Since the fluid moved very slowly outside the onion-like structure compared to the movement inside, the boundary of the structure could be easily determined from the movement of the fluid, as shown in Figure 6. The top and bottom points of the structure were determined from the boundary above and below the impeller tip, while the outer edge was inferred from the boundary at the middle height corresponding to the top and bottom edges of the impeller.

The onion-like structure developed mainly in the radial direction until it touched the vessel wall, while the height saturated at roughly 30% of the liquid height. These results were largely dependent on both impeller geometry and rheological properties of the surfactant solution. The paddle impeller used generated strong radial and weak axial discharge flows. It is also well known that a pair of circulating flows is formed for less viscous Newtonian fluids, while for viscoelastic fluids, the discharge flow is retarded by the elastic force and a secondary flow develops as explained above.

Since the time scale of expansion and contraction was comparable to the time scale of blade passage at 20 rpm, the fluid was not discharged from the impeller region and the width of the structure was equivalent to that of the impeller. When the height of the structure was larger than the impel-

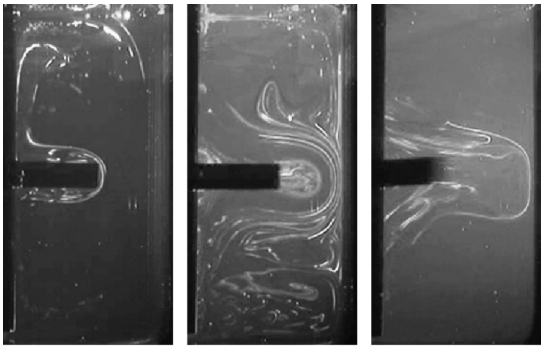

Fig. 7 Development of onion-like structure with an increase in the rotational speed. The solution with C_S=2000 ppm and ξ=2 was agitated at rotational speeds of (a) 20, (b) 60, and (c) 100 rpm

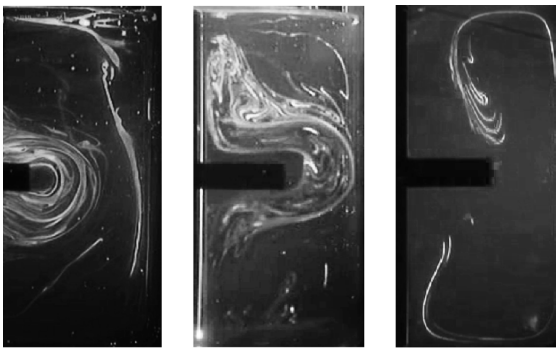

Fig. 8 Onion-like structures formed in solutions with various surfactant concentrations for ξ=2: (a) C_S=1000 ppm at 10 rpm, (b) C_S=2000 ppm at 50 rpm, and (c) C_S=4000 ppm at 80 rpm

ler thickness, the fluids above and below the impeller rotated with the impeller (**Figure 7**(a)). With increasing rotational speed, the fluid was pushed outward from the impeller just before the blade passage and it subsequently returned to the impeller region. As a result, the width of the structure fluctuated between the diameters of the impeller and vessel. Thus, the fluid was deformed not only in the radial direction but also in the axial direction. The axial expansion seemed to be restricted because of the limitation on the radial expansion by the vessel wall. Therefore, the height of the structure reached a maximum before the blade passage and returned to the original value at 20 rpm (Figure 7(b)). Finally, the onion-like structure always touched the vessel wall at 100 rpm, and thereafter the width did not fluctuate anymore because the discharged fluid could not return to the impeller region between blade passages. Similarly, although the height was still fluctuated, it reduced to that at 20 rpm because the onion-like structure did not develop appreciably in the axial direction (Figure 7(c)).

A cavern formed in a yield stress fluid increases in size with an increase in the rotational speed, but its dimensions are usually stable under constant agitating conditions. In contrast, the onion-like structure is easily deformed depending on the blade passage at a constant rotational speed and becomes unstable at large rotational speeds. Therefore, a smaller rotational speed is favorable when utilizing characteristic fluid flows for manufacturing novel materials.

2.5 Effect of surfactant concentration on onion-like structure

Finally, the effect of the surfactant concentration on the fluid flow and the onion-like structure is discussed. As shown in Figure 1, the zero-shear viscosity was not affected by the surfactant concentration, but the viscosity began to decrease at a lower shear rate for a solution with a lower surfactant concentration. Thus, the higher the solution concentration is, the more difficult it is to fluidize the solution. On the other hand, the viscoelasticity is intricately influenced by both number of micellar entanglements and applied shear rate. At a high concentration, the first normal stress difference will increase drastically but a high shear rate is required for deforming the micellar networks.

The tracer fluid was injected near the mixing shaft for solutions with different concentrations, and the resultant colored regions are shown in **Figure 8**. The molar ratio of counterions to surfactant was constant at 2. At C_S=1000 ppm, a large and stable onion-like structure was observed even at a rotational speed of 10 rpm. This is because the elastic force is significant compared to the viscous one at a small shear rate. For the 1000 ppm solution, the onion-like structure was observed at 6 rpm and the relaxation time was predicted to be 8 s from our study. Thus, the criterion for the formation of onion-like structure was We=3.2, which is close to 1.0. With increasing rotational speed, the onion-like structure increased in size while maintaining the stability but did not touch the vessel wall even at 50 rpm. On the other hand, the colored pattern of the 4000 ppm solution was similar to that of the 2000 ppm solution for ξ=5 (Figure 4(b)). The tracer fluid was instantaneously pushed out in radial direction from the impeller edge resulting in the fluid having a circular flow. The onion-like structure could not be observed for the 4000 ppm solution at any of the rotational speeds investigated, while the dark part was pushed out from the impeller edge at speeds greater than 80 rpm in the slit light visualization, similar to Figure 3(c). Since the 4000 ppm solution had a relaxation time of 0.1 s, similar to the 2000 ppm solution with ξ=5, a dark part was generated at We=0.5, which is of the same order as unity.

The results obtained so far suggest that the condition $We \geq 10°$ is necessary but not sufficient for the formation of an onion-like structure. This is because the onion-like structure becomes unstable and will be destroyed when a significant inertia force is acting on it. Here, the effect of the inertia force was evaluated by considering both Reynolds number, Re, and Elasticity number, El. The elasticity number is the ratio of elastic force to inertia force, and the Weissenberg number is the ratio of elastic force to viscous force. Hence, these dimensionless numbers have the following relationship.

$$El = We / Re \tag{2}$$

Table 1 Dimensionless numbers at the minimum rotational speed required for generating a dark part

Cs [ppm]	ξ [—]	τ_r [s]	η [Pa·s]	N_{min} [rpm]	$\dot{\gamma}_{app}$ [s^{-1}]	We [—]	Re [—]	El [—]
1000	2	8	0.025	6	1.0	3.2	5.8×10	5.5×10^{-2}
2000	2	2	0.028	20	3.3	2.7	1.7×10^{2}	1.6×10^{-2}
4000	2	0.1	0.031	80	13	0.5	6.2×10^{2}	8.6×10^{-4}
2000	5	0.1	0.0028	150	25	1.0	1.3×10^{4}	7.8×10^{-5}

In order to calculate the Reynolds number for a non-Newtonian fluid, knowledge of the representative shear rate in the system of interest is necessary. The apparent shear rate in the whole vessel $\dot{\gamma}_{app}$ was calculated using the Metzner-Otto relation (Metzner and Otto, 1957) expressed by Eq. (3).

$$\dot{\gamma}_{app} = B(N/60) \tag{3}$$

A B value of 10 was used for paddle impeller, which is the mean value obtained in a previous numerical simulation (Kaminoyama *et al.*, 2011). At the apparent shear rate, the viscosity was interpolated from Figure 1 to calculate the Reynolds number. The dimensionless numbers and corresponding variables at N_{min} are tabulated in **Table 1**. From the fact that the onion-like structure was observed only for rotational speeds greater than N_{min} for the solutions with concentrations of 1000 and 2000 ppm for $\xi=2$, the condition required to form the structure can be written as follows:

$$We \gtrsim 1 \quad \text{and} \quad El \gtrsim 10^{-2} \tag{4}$$

These conditions imply that the onion-like structure will be build when the elastic force is comparable to the viscous one and is not much smaller than the inertia force.

Conclusions

The viscoelasticity of a surfactant solution can be easily controlled by varying the concentrations of the surfactant and counterions. In this study, we have investigated the effect of the concentrations on the fluid flow in a mixing vessel by using a paddle-type impeller. If the solution has significant elasticity and relatively high viscosity, a radial discharged fluid lump first spirals up along the isolated mixing core region because of the elasticity and then spirals down along the core region owing to the centrifugal force. Hence, a core-shell-structure flow, called onion-like structure in this study, is formed around the impeller. It is found that the onion-like structure is formed when the elastic force is larger than the viscous force ($We>1$) and is not negligible compared to the inertia force ($El>0.01$). Moreover, a stable onion-like structure can be realized by operating the impeller at a small rotational speed as much as possible or by using a fluid with a long relaxation time. Finally, since the fluid in the shell is stretched along the core region and will not mix with the fluid in the core, it might be possible to generate crystals having large aspect ratios. Furthermore, the crystals can be easily separated from the liquid phase by reducing viscoelasticity through the addition of counterions.

Nomenclature

B	=	constant in the Metzner–Otto relation	[—]
C_S	=	surfactant concentration	[ppm]
D	=	inner diameter of mixing vessel	[m]
El	=	slasticity number ($=We/Re$)	[—]
H	=	height of onion-like structure	[m]
N	=	rotational speed of impeller	[rpm]
N_1	=	first normal stress difference	[Pa]
n	=	number of blades	[—]
Re	=	Reynolds number ($=\rho(N/60)D^2/\eta$)	[—]
W	=	width of onion-like structure	[m]
We	=	Weissenberg number ($=n(N/60)\cdot\tau_r$)	[—]
$\dot{\gamma}_{app}$	=	apparent shear rate in a mixing vessel	[s^{-1}]
η	=	viscosity	[Pa·s]
ρ	=	density	[kg/m^3]
τ_r	=	relaxation time	[s]
ξ	=	molar ratio of counterion to surfactant	[—]

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