Effect of Molar Concentration Ratio on the Flow Properties of Rod-Like Micellar Solutions Passing through Small Orifices

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The flow properties of rod-like micellar (surfactant) solutions passing through circular orifices with an inner diameter of 100 µm to 1.0 mm were investigated in this study. Rod-like micellar solutions comprising a cationic surfactant [oleyl bis(2-hydroxyethyl)methylammonium chloride; Lipothoquad O/12] and a counterion (sodium salicylate; NaSal) were used. The molar concentration ratio was varied from 0.10 to 100 to change the rheological properties of the test fluid, which were evaluated using a strain-controlled rheometer and a capillary viscometer. All the rod-like micellar solutions exhibited non-Newtonian viscosity except those with molar concentration ratios of 0.10 and 0.15, which instead exhibited Newtonian viscosity consistent with that of water. In the dynamic viscoelasticity measurements, the relaxation times of the rod-like micellar solutions with molar concentration ratios other than 0.10, 0.15, and 100 were calculated by extrapolating slopes 1 and 2. For each orifice, the experimental results with water alone agreed with theoretical predictions within the experimental errors (thereby demonstrating the validity of the experimental setup). In dimensionless graphs arranged by generalized Reynolds number, the dimensionless pressure drops for the molar concentration ratios of 0.10, 0.15, 50, and 100 agreed well with the experimental (predicted) values for water. For the other rod-like-micellar solutions, the dimensionless pressure drop was larger than that for water. In other words, the rheological and flow properties were found to change with the molar concentration ratio. To discuss the experimental results in depth, the flow resistivity was calculated and was largest for the molar concentration ratio of 1.0. The increase in pressure drop was also largest for molar concentration ratio of 1.0. The Weissenberg number was used to summarize the experimental results in terms of elastic properties, and the characteristic increase in pressure drop was found to occur at a Weissenberg number on the order of $10^3$, at which elasticity was strongly expressed.

Key Words: Orifice / Pressure drop / Micellar solution / Molar concentration ratio / Rod-like micelle

1. INTRODUCTION

Complex fluids have been studied in the field of fluid engineering to serve many applications, and a characteristic of a complex fluid is that it behaves peculiarly even as a dilute solution of not more than 100 ppm. For example, surfactant solutions exhibit drag reduction that reduces the frictional losses of turbulent flows,1,2 which is known to be due to rod-like (worm-like) micelles in the solutions.3 The surfactant solutions comprise surfactant molecules consisting of hydrophilic and hydrophobic groups, and above a certain concentration (known as the critical micelle concentration) spherical micelles form, which are aggregates of surfactant molecules.4 Also, rod-like micelles form upon adding counterions (salts) to a surfactant solution containing spherical micelles, and the rod-like micelles form a network structure that causes remarkable viscoelasticity in shear flow.5 It is widely known that this micellar structure suppresses turbulent eddies and thus reduces frictional resistance.3 Surfactant solutions have been used in practice as an energy-saving technology for liquid transportation in circulatory pipelines because they cause less shear-induced mechanical degradation compared with polymer solutions, despite both surfactant solutions and polymer solutions being viscoelastic fluids (in a polymer solution, shear breaks the polymer chains, thereby degrading the rheological properties appreciably).6,7 This is a major feature of surfactant solutions of rod-like micelles (rod-like micellar solutions), and the flow properties of rod-like micellar solutions have been studied previously.8–11
cations in pipelines. There have been relatively few studies in which the order of magnitude of the characteristic length was less than $10^{-4}$ m (100 µm), with studies tending to go only as small as $10^{-5}$ m (1 mm).\(^{12,13}\) Flows with a small characteristic length have interesting features when considered in terms of dimensionless numbers. The dimensionless Reynolds number $Re$ is the ratio between the inertial and viscous forces, namely,

$$Re = \frac{\rho V D}{\mu},$$

(1)

where $\rho$ is the density, $\mu$ is the (Newtonian) viscosity, $V$ is the characteristic velocity, and $D$ is the characteristic length. The dimensionless Weissenberg number $Wi$ is the ratio between the elastic and viscous forces:

$$Wi = \lambda \dot{\gamma}.$$  

(2)

Here, $\lambda$ is the relaxation time and $\dot{\gamma}$ is the strain rate. For constant characteristic velocity, the smaller the characteristic length, the smaller $Re$ (which usually corresponds to laminar flow), whereas the strain rate and $Wi$ are larger under the same conditions. In other words, dilute aqueous solutions with low viscoelasticity are characterized by strongly expressed elastic properties ($Wi > 10^3$) even for small relaxation times (often $\lambda < 10^{-2}$ s). Therefore, many previous studies of complex fluids with dilute concentrations used flow fields with small characteristic lengths (often not more than 1 mm).\(^{14,15}\) For example, Watanabe et al. reported reduced frictional losses in dilute polymer solutions of 5 ppm polyethylene oxide (PEO) and 3 ppm polyacrylamide (PAA) in capillary (inner diameter: 148.4-251.8 µm) with low $Re$ ($Re < 5.0 \times 10^3$).\(^{14}\) Referring to flows with characteristic lengths of not more than 100 µm, microfluidics differs from normal-scale fluid dynamics and has led to interesting findings.\(^{16}\) For example, Yasuda et al. studied the elongation of vortices of PAA passing through a rectangular channel of height 1.66 mm or 35 µm; they found that the vortex elongation depended on the shear rate and the slip between the polymer solution and the channel wall. However, studies differ in their definition and interpretation of microfluidics; herein, a characteristic length of not more than 100 µm is defined as being microscopic.

Regarding the flow geometry, there have been many studies of shear flow in circular and rectangular tubes.\(^{17-19}\) This is because shear flow pertains to pipelines and the simple Couette flow in rheometers used to understand the rheological characteristics of test fluids, and much knowledge has been obtained.\(^{20,21}\) However, elongational flows have been studied far less than have shear flows. To understand the physical properties of a fluid, one must measure its stress while subjecting it to a constant strain or strain rate, or measure its strain and strain rate while a constant stress is applied. Because it is relatively easy to subject a fluid to a shear strain or shear rate, the shear stress can be measured precisely. By contrast, it is very difficult experimentally to subject a fluid to elongation only (i.e., no shear), and therefore the method of extending simple shear flows has been used instead to study elongational flows. Examples include flow fields with constant elongational rates using a hyperbolic shape [Fig. 1(a)], a stagnation point [Fig. 1(b)], and an abrupt contraction and expansion with slits or orifices in a rectangular or cylindrical channel [Fig. 1(c)]. These flow fields have been used to obtain knowledge about elongational properties.\(^{22,23}\) For example, García et al. measured the elongational viscosity and pressure drop in a hyperbolic abrupt-contraction-and-expansion flow using surfactant solutions, suggesting that micelles in surfactant aqueous solutions may be destroyed by the development of a peculiar flow phenomenon (corner vortices) upstream.

As mentioned above, there have been few reports on elongational flows of surfactant solutions (especially those with small characteristic lengths). There have been even fewer studies of flow fields with rectangular orifices (slits) that could be used for optical rheometry, which is essential for understanding the micellar structure. Ushida et al. previously studied a cationic surfactant solution of cocoyl alkytrimethyl ammonium chloride (Lipoquad C-50) used to vary the molar concentration ratio (molar concentration of counterions relative to...
molar concentration of surfactant solution), and they reported its effect on the pressure drop as it passed through a small orifice. Characteristic flow properties were obtained in which the pressure drop was higher for surfactant solutions with a specific molar concentration ratio and diameter of not more than 1.0 mm. It was also reported that the singular flow properties did not appear when the diameter was 1.0 mm, which is a characteristic of a small-scale flow. Furthermore, a cationic surfactant solution of oleyl bis(2-hydroxyethyl)methylammonium chloride (Lipothoquad O/12) was used under the same experimental conditions. It was important to consider the non-Newtonian viscosity and elastic properties, and to organize terms of characteristic length. Kato et al. measured the shear flow properties and elongational flow properties in polymer solutions are presented based on rheological properties of PEO and PAA. Ushida et al. investigated the rheological properties (first normal stress difference and dynamic viscoelastic measurement) and frictional loss of Lipoquad C-50 and Lipothoquad O/12, and reported increased viscoelasticity and drag reduction rate due to the increase in counterions, as well as the formation of aggregate structures under non-shear conditions. Lin et al. investigated the effects of Lipothoquad O/12 on shear viscosity, elongational viscosity, and dynamic viscoelasticity when the concentration and molar concentration ratio of Lipothoquad O/12 were varied. Kadoma et al. measured the flow properties of cetyltrimethylammonium bromide (CTAB) with counterion sodium salicylate (NaSal) with molar concentration ratio varying from 1 to 8 by small-angle light scattering and showed that the increased counterion content at a specific molar concentration ratio promoted flexibility. It was reported that Lipothoquad O/12 with molar concentration ratio varying from 1.5 to 100 had multiple relaxation times. Meng et al. revealed the relationship between frictional loss and wall shear rate of carboxymethylcellulose in a circular tube flow (inner diameter: 100-500 µm) and reported that the effects of surface tension, wall slip, and polymer chain size were negligible. Lu et al. reported drag reduction using Lipoquad C-50 in turbulent flows with a diameter of 6 mm and $Re \geq 1.0 \times 10^4$. Usui et al. reported drag reduction using Lipothoquad O/12 in a circular tube with an inner diameter of 11.4 mm, and Hashimoto et al. reported increased wall shear stress with increasing molar concentration ratio in a circular tube with an inner diameter of 1.14 mm using CTAB. The pressure drop was larger for surfactant solutions with a molar concentration ratio of 1 or higher compared with a molar concentration ratio of 0.667. Ushida et al. showed pseudo-laminarization in capillary flow (inner diameter: 133 µm to 2.87 mm) using Lipoquad C-50 and Lipothoquad O/12, with laminar flow being maintained up to a maximum $Re$ of $4.0 \times 10^3$ at a specific molar concentration ratio, and they reported that the disappearance of this phenomenon was consistent with the wall shear rate at which the non-Newtonian viscosity disappears. Rodd et al. studied the flow properties in abrupt-contraction-and-expansion flows with a contraction ratio of 16 using PEO and reported that (i) unstable vortices formed upstream and (ii) the pressure drop increased in response to the values of $Re$ and $Wi$. Li et al. conducted experiments with varying concentrations of PEO with different molecular weights in abrupt-contraction flows with a channel height of 45 µm and a contraction ratio of eight. Lanzaro et al. studied the behavior of vortices generated upstream of a microfluidic channel (height: 47 µm; width: 50 µm to 0.8 mm) with an abrupt contraction using PAA. Ushida et al. measured the pressure drop through small orifices (inner diameter: 100 µm to 1.0 mm) using Lipoquad C-50 with molar concentration ratios varying from 0.10 to 10.0 and studied the flow properties. For not more than 500 µm, the Lipoquad C-50 at a molar concentration ratio of 1.0 exhibited a larger pressure drop than that with water alone. In addition, a simple visualization experiment was performed and the relationship between the pressure drop and the unstable vortices upstream was discussed. Furthermore, they used Lipoquad C-50 (molar concentration ratio: 1.0) and Lipothoquad O/12 (molar concentration ratio of 1.5) to measure the pressure drop when passing through small orifices (inner diameter: 100 µm to 1.0 mm), reporting that Lipoquad C-50 showed similar results to those from previous studies in that the pressure drop was larger than that with water when passing through micropores with an inner diameter of not more than 500 µm, and that Lipothoquad O/12 always showed a larger pressure drop than that with water in the measured range of $Re$ ($8.5 \times 10^3 \leq Re \leq 5.8 \times 10^5$). The mechanism for the increased pressure drop was discussed for $Wi > 10^6$.

The rheological properties (viscosity and relaxation time) of complex fluids strongly depend on the concentration and concentration ratio. In terms of engineering applications of
shear flows, drag reduction in flows in circular tubes has been studied. Meanwhile, for polymer solutions, the pressure drop and the flow behavior upstream of the channel have been found to be affected by the flow properties (contraction ratio in the slit), fluid properties (concentration and rheological properties), and dimensionless numbers ($Re$ and $Wi$). However, there is less knowledge regarding rod-like micellar solutions than there is regarding polymer solutions. As mentioned earlier, there have been many studies of the flow properties of surfactant and polymer solutions; however, these tended to involve shear flows, with little being known about elongational flows. There have been some studies of polymer solutions in elongational flow, but those of rod-like micellar solutions have overwhelmingly involved shear flow, with elongational flow very rarely reported. In work previous to the present study, Ushida et al.\textsuperscript{24,25) reported useful findings regarding rod-like micellar solutions in flows through microscopic orifices; of particular interest was the increased pressure drop at certain values of the molar concentration ratio between surfactant solution and counterion. However, the phenomenon was related to a specific surfactant solution, and the experimental results were not generalized. The purpose of the present study was to measure the pressure drop in surfactant solutions flowing through small orifices for surfactant solutions different from that used in the previous studies and to obtain new knowledge about the generality of the singular flow properties.

2. TEST FLUIDS

2.1 Water

The water used in the study was deionized water (electrical resistivity: 18.2 MΩ·cm) that had been passed through an ion-exchange resin by a distillation apparatus (RFD240NC; ADVANTEC Co. Ltd.).

2.2 Surfactant solution of rod-like micelles

Oleyl bis(2-hydroxyethyl)methylammonium chloride (Lipothoquad O/12; Lion Specialty Chemicals Co., Ltd.) was used as a cationic surfactant solution; the molecular weight was 405.8 g/mol and the molar concentration $C_s$ was $1.2 \times 10^{-2}$ mol/L.\textsuperscript{25) The formation of rod-like micelles requires the addition of counterions, which in the present study were sodium salicylate (NaSal; Wako Pure Chemical Industries Co., Ltd.) with a molecular weight of 160.1 g/mol. The molar concentration ratio

$$\phi = \frac{C_c}{C_s}$$

was adjusted from 0.10 to 100 by fixing the concentration $C_s$ of Lipothoquad O/12 and varying the concentration $C_c$ of NaSal. To prepare the surfactant solution, Lipothoquad O/12 in the liquid state was dissolved in a glass beaker filled with water, and the rod-like micellar solution (Lipothoquad/NaSal) was prepared by adding and stirring NaSal in an amount corresponding to the required molar concentration ratio. For example, the preparation method for $\phi = 1.0$ was as follows: Lipothoquad O/12 was dissolved in a glass beaker filled with 5000 mL of water to a mass concentration of 0.49 wt%, then 0.19-wt% NaSal was added and stirred with an acrylic rod; the solution was left at room temperature for half a day before the experiment (to ensure complete dissolution).

3. PHYSICAL PROPERTIES

3.1 Density

Because the used rod-like micellar solutions were of (semi-)dilute concentration, the density of water ($\rho = 1.0 \times 10^3$ kg/m$^3$) was corrected according to the temperature $T$ in the experiments.
3.2 Viscosity

Viscosity is a very important physical property of a flow. In the present study, the steady-state viscosity at low shear rates \(10^{-1} \text{ s}^{-1} \leq \dot{\gamma} \leq 10^3 \text{ s}^{-1}\) was measured using a strain-controlled rheometer (ARES-G2; TA Instruments Co., Ltd.). At high shear rates \(2.7 \times 10^2 \text{ s}^{-1} \leq \dot{\gamma}_w \leq 1.0 \times 10^4 \text{ s}^{-1}\), the viscosity was measured using a capillary viscometer (distance \(L_c\) between two pressure holes: 100 mm; SUS304 stainless steel) with an inner diameter \(D_c\) of 0.90 mm. An overview of the syringe pump and pressure transducer is given in Section 3. The viscosity curves are shown in Fig. 2, where the vertical axis corresponds to the shear rate \(\dot{\gamma}\) and the wall shear rate \(\dot{\gamma}_w\) [Eq. (4)] and the horizontal axis corresponds to the shear rate \(\dot{\gamma}_w\) [Eq. (5)]:

\[
\eta = \frac{\tau_w}{\dot{\gamma}_w}, \tag{4}
\]

\[
\dot{\gamma}_w = \frac{3n + 1}{4n} \frac{8V}{D_c}, \tag{5}
\]

where \(n\) is the power-law index and \(V\) is the mean velocity passing through the capillary. Because the viscosity curves comprise many data points, they were separated into two graphs [Fig. 2(a) and (b)]. The viscosities of water alone and the micellar solutions with \(\phi = 0.50, 1.0, 1.5, 10, 15, 30, 50, \text{ and } 100\) are Newtonian \((\mu = 1.0 \times 10^{-3} \text{ Pa·s})\). Because the viscosities of the micellar solutions with \(\phi = 0.50, 1.0, 1.5, 10, 15, 30, 50, \text{ and } 100\) are non-Newtonian, a power-law model [Eq. (6)] in the form of a power-law relationship between the wall shear stress \(\tau_w\) [Eq. (7)] and the wall shear rate was used to calculate the dilatant viscosity \(m\) and the power-law index \(n\):

\[
\tau_w = m (\dot{\gamma}_w)^n, \tag{6}
\]

\[
\tau_w = \frac{D_c \Delta p}{4L_c}, \tag{7}
\]

Table II Relaxation time of rod-like micellar solutions.

| Test fluids | Temperature, \(T\) [°C] | Relaxation time, \(\lambda\) [s] |
|-------------|-------------------------|-------------------------------|
| \(\phi = 0.50\) | 20.0 | \(2.0 \times 10^{-2}\) |
| \(\phi = 1.0\) | 20.0 | \(1.1 \times 10^{0}\) |
| \(\phi = 1.5\) | 20.0 | \(6.0 \times 10^{-2}\) |
| \(\phi = 10\) | 20.0 | \(6.3 \times 10^{-3}\) |
| \(\phi = 15\) | 20.0 | \(1.1 \times 10^{-2}\) |
| \(\phi = 30\) | 20.0 | \(3.2 \times 10^{-2}\) |
| \(\phi = 50\) | 20.0 | \(1.8 \times 10^{-3}\) |

The values of \(m\) and \(n\) calculated using Eq. (8) are given in Table I.

3.3 Relaxation time

The relaxation time is an indicator of elastic properties. Each micellar solution was subjected to dynamic rheological measurements using a strain-controlled rheometer (ARES-G2; TA Instruments Co., Ltd.) at a temperature \(T\) of 20 °C. Measurements were performed to confirm the linearity of the storage modulus \(G'\) and loss modulus \(G''\). The strain conditions under which \(G'\) and \(G''\) were linear were all 100 % except for \(\phi = 1.5\) (30 %). Figure 3 shows the storage modulus \(G'\) and loss modulus \(G''\) plotted against the angular frequency \(\omega\). Because \(G'\) and \(G''\) did not intersect in the range of measured angular frequency, the relaxation time was calculated as the inverse of the angular frequency at the intersection of the solid
(gradient = 2) and dashed (gradient = 1) lines in the figure. Consequently, the relaxation times $\lambda$ were as given in Table II. Because the micellar solutions with $\phi = 0.10, 0.15, \text{and } 100$ did not exhibit a linear range, the corresponding relaxation time could not be obtained.

## 4. EXPERIMENTAL SETUP

### 4.1 Experimental apparatus

The experimental apparatus is shown schematically in Fig. 4(a). A cylindrical channel with a small orifice at its far end was used as the flow channel. A syringe pump was used with a constant flow rate. The test fluid flowed through the cylindrical channel and small orifice into the vessel storing...
the water. The pressure drop passing through the small orifice was measured via a differential pressure transducer connected to the side of the cylindrical channel and a pressure hole in the side of the vessel. There follows an overview of the experimental setup.

### 4.2 Orifices

Three different small orifices were used as follows: (i) inner diameter $D = 1.0 \text{ mm}$ (thickness $L = 1.0 \text{ mm}$); (ii) $D = 500 \mu \text{m} \ (L = 500 \mu \text{m})$; (iii) $D = 100 \mu \text{m} \ (L = 20 \mu \text{m})$. The orifices with $D = 1.0 \text{ mm}$ and $500 \mu \text{m}$ were machined in SUS304 stainless steel [Fig. 4(b) and (c)], whereas that with $D = 100 \mu \text{m}$ was a commercially made pinhole in nickel [PA-100; Sigma Koki Co., Ltd.; Fig. 4(d)]. The material containing each small orifice was bonded to a base plate (inner diameter: 10 mm; SUS304 stainless steel) using an epoxy-based adhesive and attached to the cylindrical channel. Because the orifice with $D = 100 \mu \text{m}$ was in foil, the latter overlapped the base (inner diameter: 3 mm; SUS304 stainless steel) and was glued to it [Fig. 4(e)]. It has been reported that the shape of the orifice with $D = 100 \mu \text{m}$ differed between the front and back sides.\textsuperscript{24} However, the difference was negligible at the pressure drops associated with water alone and the micellar solution with $\phi = 1.5$ (see Appendix 1).

### 4.3 Cylindrical channel

The flow channel was a cylindrical acrylic channel (inner diameter: 25 mm; length: 180 mm) in which a pressure hole (diameter: 10 mm) had been drilled 150 mm upstream from the outlet.

### 4.4 Syringe pump

A high-pressure micro-feeder (JP-H3, JP-H5; Furue Science Co., Ltd.) was used as a syringe pump, this being similar to the syringe pumps used in previous studies.\textsuperscript{24, 25} Two syringes (100 mL and 17 mL) were used interchangeably depending on the required flow rate. The syringes were made of SUS304 stainless steel. The flow rate $Q$ of the syringe pump was adjusted by turning a dial, and the calibration used to calculate $Q$ is given in Appendix 2. The error in the flow rate was less than 4%.

### 4.5 Vessel

An acrylic vessel with internal dimensions of 350 mm $\times$ 350 mm $\times$ 310 mm (thickness: 10 mm) was used to store the water.

### 4.6 Pressure transducers

Differential pressure transducers (SDP-11, SDP-12; Tsukasa Sokken Co., Ltd.) were used to measure the pressure drop. Three different differential pressure transducers with ranges of 500 Pa (SDP-11), 10 kPa (SDP-12), and 100 kPa...
(SDP-12) were used interchangeably depending on the values of the pressure drop. The pressure transducers were calibrated as follows. First, a pressure hole was made in the bottom of each of two cylindrical tanks (diameter: 50 mm) with uniform cross-sectional areas and connected to the pressure transducer. The two tanks were then adjusted so that their water levels were the same, and the pressure transducer was zeroed. Differential pressure is measured as the head difference corresponding to an arbitrary pressure. The calibration results are given in Appendix 3. The 500-Pa and 10-kPa pressure transducers were both found to have errors of less than 5.0%. A Bourdon pressure gauge (measuring range: 0.1 MPa; Yamamoto Keiki Manufacturing, Co., Ltd.) was installed at the connection between the flow channel and the head tank to measure pressure at 100 kPa, because measurement was difficult by the method described above. The 100-kPa differential pressure gauge was found to have an error of less than 5.0%. Because of poor accuracy, the results exclude data obtained at pressures below 1 Pa.

### 4.7 Experimental method

The pressure drop was measured as follows. 1) The differential pressure gauge was connected to the pressure ports in the sides of the flow channel and vessel by Teflon tubing, and the cylindrical channel and syringe pump were connected likewise. 2) The chosen small orifice was attached to the far end of the cylindrical channel, and test fluid was drawn into the syringe pump until full. Any air bubbles were removed by the head difference, and the flow channel was checked to ensure that it too was free of air bubbles. 3) The electrical signal from the pressure transducer was recorded by a PC as a voltage value, and the voltage before the flow was set to zero. 4) The test fluid flowed at the constant flow rate determined by the setting of the syringe pump, and the output voltage from the pressure transducer was measured and recorded as text data. In this study, the experiments were conducted with the flow rate being adjusted from small to large; however, preliminary experiments confirmed that the measured flow properties were independent of the direction of flow-rate variation.

### 5. EXPERIMENTAL RESULTS

#### 5.1 Definitions of dimensionless numbers

The experimental results are organized in two types, namely, dimensional flow curves and dimensionless flow curves. The dimensional flow curves comprise the experimental results organized by pressure drop $\Delta p$ on the vertical axis and apparent strain rate $\dot{\gamma}_{\text{app}}$ [Eq. (9)] on the horizontal axis, where $V$ is the mean velocity [Eq. (10)], $D$ is the diameter, and $Q$ is the flow rate:

$$V = \frac{4Q}{\pi D^2}. \tag{10}$$

The dimensionless flow curves comprise the experimental results organized as follows: the vertical axis corresponds to the dimensionless pressure drop $K$ [pressure drop divided by dynamic pressure due to mean velocity; Eq. (11)] and the horizontal axis corresponds to $Re$ [Eq. (1)], where $\rho$ is the density and $\mu$ is the Newtonian viscosity:

$$K = \frac{2\Delta p}{\rho V^2}. \tag{11}$$

For the rod-like micellar solutions that exhibited non-Newtonian viscosity, we use the generalized Reynolds number $Re^*$ [Eq. (12)] using the power-law model proposed by Harris,\textsuperscript{39, 40} where $m$ is the dilatant viscosity and $n$ is the power-law index:

$$Re^* = \frac{\rho V^{2-n} D^n}{m \left( \frac{3n+1}{4m} \right)^{n-1} 8^{n-1}}. \tag{12}$$

#### 5.2 Prediction

Previous studies\textsuperscript{41, 42} have reported the following expression for predicting $K$ for flow through a small orifice:

$$K = 2.2 + \frac{37.7}{Re^*} + \frac{64}{Re} \cdot \frac{L}{D}. \tag{13}$$
Also, by applying dynamic pressure to Eq. (13), we obtain
\[
\Delta p = K \cdot \frac{1}{2} \rho \dot{V}^2 .
\]  
(14)

Shown as a solid line in the plotted results, the predicted values of \(K\) and \(\Delta p\) are compared with the experimental results. Moreover, a previous study\(^{43}\) has reported the pressure drop \(\Delta p_L\) (corresponding to the pressure drop across an orifice) and dimensionless pressure drop \(K_L\) for flow through rectangular apertures, namely
\[
\Delta p_L = \Pi \frac{\mu Q}{8D^3} ,
\]  
(15)
\[
K_L = \frac{64}{Re} \cdot \frac{L}{D} ,
\]  
(16)

where \(\Pi\) is a shape coefficient, with \(\Pi = 1\) in the case of small orifices. The above equations correspond to the theoretical values for laminar flow and are shown as a dotted line in the plotted results.

### 5.3 Water

The experimental results for water alone are shown in Appendix 4. The experimental errors for the dimensionless pressure drop (Table III) were estimated from the various measurement errors and are shown as error bars in the experimental results:
\[
\frac{\delta K}{K} = \frac{\delta(\Delta p)}{\Delta p} + 2 \frac{\delta Q}{Q} + 4 \frac{\delta D}{D} + \frac{\delta \rho}{\rho} .
\]  
(17)

For water alone, the experimental results for each small orifice agree with the predictions within the experimental errors in the measured ranges of apparent strain rate \((1.5 \times 10^4 \text{ s}^{-1} \leq \dot{\gamma}_{\text{app}} \leq 4.1 \times 10^5 \text{ s}^{-1})\) and \(Re\) \((8.2 \times 10^5 \leq Re \leq 2.7 \times 10^9)\). Therefore, the experimental method and apparatus are highly reasonable.

### 5.4 Micellar solutions

The experimental results for the rod-like micellar solutions are shown in Figs. 5 and 6. For \(D = 1.0 \text{ mm}\), there is approximate agreement between the measured \(\Delta p (K)\) and the prediction in ranges of \(1.5 \times 10^4 \text{ s}^{-1} \leq \dot{\gamma}_{\text{app}} \leq 1.0 \times 10^5 \text{ s}^{-1}\) and \(8.2 \times 10^5 \leq Re^* \leq 1.2 \times 10^8\) for \(\phi = 0.10, 0.15, 50,\) and \(100\). For \(\phi = 0.50, 1.0, 1.5, 10, 15,\) and \(30\), \(\Delta p\) and \(K\) are always larger than the predicted values. However, \(K\) in the dimensionless flow curve decreases gradually as \(Re^*\) increases. For \(D = 500 \mu\text{m}\), all the test fluids show the same trend as that for \(D = 1.0 \text{ mm}\); for \(D = 100 \mu\text{m}\), \(\Delta p\) and \(K\) show the same values as the predicted values for \(\phi = 0.10, 0.15,\) and \(100\) as for \(D = 1.0 \text{ mm}\) and \(500 \mu\text{m}\), while for \(\phi = 50\), the values are larger than the predicted values. Furthermore, for \(\phi = 10\), the experimental data are larger than the predictions in the dimensionless flow curve in range of \(Re^* \leq 1.0 \times 10^3\).

### 6. DISCUSSION

#### 6.1 Increase in pressure drop

Previously, Ushida et al.\(^{24}\) reported that rod-like micellar solutions (Lipoquad C-50) with molar concentration ratios from 0.10 to 10 showed an increase in pressure drop when they passed through small orifices with \(D < 1.0 \text{ mm}\) only.
Fig. 6 Dimensionless pressure drop $K$ versus Reynolds number $Re$ (Newtonian viscosity) and generalized Reynolds number $Re^*$ (non-Newtonian viscosity) for $D = (a) 1.0$ mm, (b) 500 $\mu$m, and (c) 100 $\mu$m.

when $\phi = 1.0$. As described, that situation differs from the present experimental results. In other words, it was found that the specific flow characteristics confirmed at a specific molar concentration ratio depended on the type of surfactant. In case of Lipoquad C-50, the pressure drops were changed only when $\phi = 1.0$. On the other hand, the pressure drops were changed for a specific range of molar concentration ratios ($\phi = 0.50 \sim 30$). It was thought that was the difference in chemical structure (Lipothoquad O/12; C$_{16}$H$_{33}$CH$_3$C$_2$H$_4$OHCl, Lipoquad C-50; C$_{16}$H$_{33}$NiCH$_2$Cl) was attributed. Usui et al. reported the high drag reduction effect of Lipothoquad O/12, which had a double-structure in the hydrophobic group, when using capillary flows. Furthermore, they discussed the importance of the double-structure in the hydrophobic group.

For Lipoquad C-50, which had a different chemical structure, they reported that the temperature-dependence was relatively strong and a usable temperature range was existed. Thus, the different experimental results between Lipothoquad O/12 used in the study and Lipoquad C-50 used in our previous study.

### 6.2 Flow resistivity

The dimensional and dimensionless pressure drops of the rod-like micellar solutions passing through the small orifices were found to differ depending on the specific molar concentration ratio and diameter (characteristic length). Therefore, we discuss the increase rate (flow resistivity) relative to the predicted value. The flow resistivity $R$ is defined by

$$R = \frac{K_{\text{micellar}} - K_{\text{pre}}}{K_{\text{pre}}}$$

and the flow resistivity organized by $Re$ is shown in Fig. 7. For $\phi = 0.10, 0.15, 0.50, 50,$ and 100, $R$ is almost identical to the predicted values for $D = 1.0$ mm and 100 $\mu$m; for $\phi = 1.0, 1.5, 10, 15,$ and 30, both are different ($R$ increases for $D = 100 \mu$m compared to $D = 1.0$ mm); for $\phi = 1.0, R$ is the largest in both cases; for $\phi = 1.5, 10, 15,$ and 30, $R$ is smaller for $D = 1.0$ mm compared to $\phi = 1.0,$ while for $D = 100 \mu$m, $R$ increases in all cases, especially for $Re^* \geq 1.0 \times 10^2$, which is almost consistent with $\phi = 1.0$. This suggests that the diameter could have an appreciable effect on the flow properties of rod-like micellar solutions at certain molar concentration ratios ($\phi = 1.0, 1.5, 10, 15,$ and 30). Next, we discuss the flow resistivity at $Re^* = 1.0 \times 10^2$, where the increase in flow resistivity is more pronounced. Regardless of the flow channel size, the dimensionless pressure drops also increase with increasing molar concentration ratio for $\phi = 0.10, 0.15,$ and 0.50. For $\phi = 1.0$, the dimensionless pressure drops are the largest among those of all the test fluids; for $\phi = 1.5$ and above, the dimensionless pressure drops decrease with increasing molar concentration ratio, and for $\phi = 100$ they are almost the same as those for $\phi = 0.10$ and 0.15. However, the values are larger for $\phi = 15$ and 30 than for $\phi = 10$. In other words, it was found that singular flow properties were exhibited at a specific molar concentration ratio. In a previous study on flow-induced birefringence in slit flow, Ushida et al. discussed that the number of micelles in an arbitrary space was important for the generation of flow-induced structure. They also proposed the degree of spatial constraint. Although there was a difference between slit and orifice, it was considered that the number of micelles had effect on the flow properties.
6.3 Elastic properties

The experimental results regarding the elastic properties are shown in Fig. 8, where the vertical axis corresponds to the dimensionless pressure drop $K$ and the horizontal axis corresponds to

$$Wi = \lambda \dot{\gamma}_{app}.$$  

For $D = 1.0$ mm, in the range of $Re$ with elevated $K$, it was found that $Wi$ was greater than $10^3$ for $\phi = 0.50$, 1.0, 1.5, 1.0, 15, and 30. Therefore, the rod-like micellar solutions used in this study were found to exhibit specific flow properties in the flow field where elastic properties are strongly expressed ($Wi > 10^3$). In previous studies, elastic instability in an abrupt contraction flow was reported. Rodd et al. and Ushida et al. reported instable vortex at upstream in an abrupt contraction section using dilute polymer solutions and rod-like micellar solutions, respectively. According to the above studies, when an unstable vortex was generated, the pressure drops were unstable and increases. The pressure drops increased although the pressure drops in this study did not become unstable. It was thought that the anomalous pressure drops were caused by the elastic instability. One of the conditions for the elastic instability was a high Weissenberg number. In this study, $Wi > 10^3$ was considered to correspond to this condition.
From the above discussions, the following generalities were obtained: rod-like micellar solutions (Lipothoquad O/12) exhibited non-Newtonian viscosity at specific molar concentration ratios. In addition, the pressure drops passing through small orifices increased at a specific molar concentration ratio. However, the experimental results were different from those of the rod-like micellar solutions with a different chemical structure (Lipoquad C-50). In other words, the singular flow properties of rod-like micellar solutions changed depending on the type of surfactant. On the other hand, the pressure drops increased when the Weissenberg number was relatively high ($\text{Wi} > 10^6$), which could be attributed to elastic instability.

7. CONCLUSIONS

This study investigated the generality of the flow properties of rod-like micellar solutions, which differed from the surfactant solutions used in previous studies, when they passed through small orifices with an inner diameter of less than 1.0 mm. The following conclusions are drawn. First, the pressure drop of water showed good agreement with the predicted values. Second, the experimental results for the rod-like micellar solutions with various molar concentration ratios showed that the pressure drops of surfactant solutions with under- or over-added counterions were the same as the experimental and predicted values for water. The pressure drops of the surfactant solutions were larger than those of water and initially increased with increasing molar concentration ratios and then tended to decrease after a certain value. Namely, singular flow properties with an increase in pressure drop at a specific molar concentration ratio were observed. In comparison with previous studies, the flow properties of the rod-like micellar solutions with different molar concentration ratios were found to be different for different types of surfactant. Third, the pressure drop of the rod-like micellar solutions at a specific molar concentration ratio increased when the characteristic length was reduced. The difference in characteristic length was clarified. Fourth, the specific flow properties of the rod-like micellar solutions with different molar concentration ratios were considered from the viewpoint of elastic properties, and it was found that the pressure drop increased in the flow field where the elastic properties were expressed strongly. Finally, the rod-like micellar solutions used in this study showed an increase in pressure drop at a specific molar concentration ratio when passing through small orifices, and the elastic properties of the rod-like micellar solutions were considered as a factor; however, the surfactant aqueous solutions used in previous studies also showed similar results. On the other hand, the range of molar concentration ratios and the magnitude of pressure drops that showed an increase in pressure drop differed from the results reported in previous studies. From these experimental results, it is concluded that the flow properties of the rod-like micellar solutions through small orifices with a diameter of less than 1.0 mm depend on the type of surfactant.

NOMENCLATURE

$C_c$ : molar concentration of NaSal (mol/L)
$C_s$ : molar concentration of Lipothoquad O/12 (mol/L)
$D$ : diameter (mm, $\mu$m)
$D_c$ : inner diameter of capillary (mm)
$G'$ : loss modulus (Pa)
$G''$ : storage modulus (Pa)
$K$ : dimensionless pressure drop (–)
$K_L$ : dimensionless pressure drop when passing through apertures (–)
$L$ : thickness of orifice (mm)
$L_c$ : distance between two pressure holes (mm)
$m$ : dilatant viscosity (Pa·s$^m$)
$n$ : power-law index (–)
$Q$ : flow rate ($m^3/s$)
$R$ : flow resistivity (–)
$Re$ : Reynolds number (–)
$Re^*$ : generalized Reynolds number (–)
$T$ : temperature (°C)
$V$ : mean velocity (m/s)
$\text{Wi}$ : Weissenberg number (–)
$\gamma$ : strain (–)
$\dot{\gamma}$ : shear rate ($s^{-1}$)
$\dot{\gamma}_{\text{app}}$ : apparent strain rate ($s^{-1}$)
$\dot{\gamma}_w$ : shear rate on wall ($s^{-1}$)
$\Delta P$ : pressure drop (Pa)
$\Delta P_L$ : pressure drop of thickness (Pa)
$\eta$ : shear viscosity (Pa·s)
$\lambda$ : relaxation time (s)
$\mu$ : Newtonian viscosity (Pa·s)
$\rho$ : density (kg/m$^3$)
$\tau_w$ : wall shear stress (Pa)
$\phi$ : molar concentration ratio (–)
$\omega$ : angular frequency (rad/s)

APPENDIX 1

The effect of the shape of the front and back of the small orifice (flow direction) on the pressure drop was studied. The
experimental results for water and a rod-like micellar solution ($\phi = 1.5$) with an orifice of $D = 100 \, \mu m$ are shown in Fig. 9. The pressure drop was found to be independent of the flow direction when the apparent strain rate ranged from $8.0 \times 10^2 \, s^{-1}$ to $1.0 \times 10^5 \, s^{-1}$. In particular, it was found that the increase in pressure drop was independent of the flow direction of the rod-like micellar solution.

**APPENDIX 2**

The syringe pump was calibrated. The actual flow rate was measured relative to the pump’s setting; the flow rate was calculated by dividing the mass of the outflow by the operating time of the pump. The calibration results are shown in Fig. 10. The error was less than 1%, and therefore the flow rate was confirmed as being the set value.

**APPENDIX 3**

Three pressure gauges (500 Pa, 10 kPa, and 100 kPa) were used in this experiment. Two types (500 Pa and 10 kPa) of differential pressure gauges that could be calibrated by head differences were tested. Figure 11 shows the output pressure $\Delta p_{\text{out}}$ for the pressure $\Delta p_{\text{appl}}$, applied by the differential head. The 500-Pa and 10-kPa pressure transducers were both found to have errors of less than 5.0%.

**APPENDIX 4**

Because of the large amount of experimental data plotted in Fig. 6, for clarity the experimental results for water alone are shown in Fig. 12. The experimental results for water agree with the predictions within the experimental errors: $D = (a)$ 1.0 mm, (b) 500 $\mu m$, and (c) 100 $\mu m$.

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Fig. 12 Dimensionless pressure drop $K$ versus Reynolds number $Re$ for water alone with $D = (a) 1.0$ mm, (b) 500 $\mu$m, and (c) 100 $\mu$m. All the pressure drops agree well with the predictions.

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