Viscoelastic Properties of Worm-like Micelle of Aluminum Tristearylate/Decahydronaphthalene

Shoichi MURATA, Akihiko TAKADA, Hiroko YAMAMOTO, and Yoshiaki TAKAHASHI

Institute for Materials Chemistry and Engineering and Department of Molecular and Material Sciences, Kyushu University, 6-1 Kasugakoen, Fukuoka 816-8580 Japan

(Received: April 30, 2008)

Temperature dependence of dynamic viscoelastic properties for 7 wt% solution of aluminum tristearylate (C18Al) in decahydronaphthalene (decalin), prepared by 2 hours heating at 130 °C and 1 day aging at room temperature, are examined. Shapes of dynamic moduli vs. frequency plots are similar to those of entangled polymer systems, implying that this system forms wormlike micelles. Temperature dependence of zero shear viscosity η° can be expressed by an Arrhenius type equation. The specific viscosities obtained at different temperature are almost constant. Plateau modulus G° gradually increases with increase of temperature T, and the values reduced by absolute temperature are almost constant. The structure examined by small angle neutron scattering and X-ray diffraction was practically the same at different T. Therefore, we conclude that as long as the sample preparation condition is maintained the same, the network structure of C18Al/decalin micelle is practically the same at different temperatures and the main relaxation process of the network is similar to entangled polymers, at least for limited conditions tested in this study.

Key Words: Aluminum Tristearylate / Decahydronaphthalene / Wormlike Micelle / Viscoelastic Properties

1. INTRODUCTION

It is well known that there are wide varieties of materials which form self-organized structure.1,2) When a sort of 3 dimensional network structure is formed, the system may possess viscoelastic properties similar to entangled polymers or gels depending on life time and strength of the structure. A typical example of low molecular weight system is wormlike micelles formed in aqueous solutions of surfactants and organic salts, such as cetyltrimethylammonium bromide and sodium salicylate (CTAB/NaSal).3-5) In this case, at least two different types of relaxation processes for network structure are known. That is, the main relaxation process for so called type II micelle is similar to entangled polymer systems, while that of type III is Maxwell type relaxation and the structure is called “phantom network”.

There also exist surfactant systems which form wormlike micelles in organic solvents.2,6) Mixtures of aluminum tristearylate (C18AI) and non-polar organic solvents, known as metal soap, are typical example of them, which show gel-like behaviors.7) However, their viscoelastic properties and structure are less studied compared to wormlike micelles in aqueous solutions. It have been reported that the viscoelastic properties of C18AI/organic solvent systems strongly depend on sample preparation conditions and aging.7) Structural analysis by light scattering and small angle X-ray scattering may be somewhat difficult for this system due to the low contrast of refractive indices and electron densities between surfactants and solvents. These may be the reasons for scarce study.

In a previous work9), we examined effects of preparation conditions and aging at room temperature on the viscoelastic properties of C18AI/decahydronaphthalene (decalin) system. First, effects of dissolving temperature and heating time are examined. The system became more uniform at higher temperature. Therefore, the dissolving temperature was fixed at 130 °C, close to the boiling temperature of decalin. Dynamic viscoelastic measurements at 25 °C after 1 day room temperature aging revealed that the longest relaxation time becomes shorter and plateau region of storage modulus becomes narrower with increase of heating time at 130 °C. The mixture became low viscosity liquid after 36 hours heating. Thus, preparation condition was fixed at 130 °C, 2 hours mixing and the difference of viscoelastic properties with the concentration was examined. Viscoelastic behavior similar to entangled polymer systems was not observed for concentrations lower than 3 wt%, while uniform solution was not obtained at concentrations higher than 10 wt%.
Aging effects are examined using C18Al, 3 wt% solution kept at room temperature. Dynamic viscoelastic properties are measured at 1, 4, and 7 days after the preparation. The values of plateau modulus and the relaxation time gradually decreased with the aging. For instance, plateau modulus obtained after 7 days aging became 1/3 of that obtained after 1 day aging. About 3 weeks later, sample solution became slightly opaque and about 2 month later, C18Al precipitated. Thus it is clear that this system is a non-equilibrium system. However, as long as the preparation condition is maintained as the same (2 hours heating at 130 °C and 1 day aging at room temperature in our study), the reproducibility of viscoelastic properties are good. It was also pointed out that pre-shear (shear rate 100 sec⁻¹ in non-Newtonian region) does not affect the data of dynamic viscoelastic properties, implying that micelles may not easily broken by the flow.

As mentioned above, viscoelastic properties similar to entangled polymer systems are observed in a limited range of C18Al concentration C (3 < C < 10 wt%) so that it is difficult to study the concentration dependence of them. In this study, we report the temperature dependence of dynamic viscoelastic properties of this system at a fixed concentration, C = 7 wt%, where typical viscoelastic properties of worm-like micelle can be examined. The structure of micelles was also examined by X-ray diffraction (XRD) and small angle neutron scattering (SANS) measurements.

2. EXPERIMENTAL

Aluminum tristearate and decahydronaphthalene (cis trans mixture) were purchased from Kishida Chemical Co. LTD, while decahydronaphthalene-d₁₈ was purchased from Aldrich. All materials were used as received. As mentioned above, C is fixed at 7 wt%, where plateau and terminal region behaviors were clearly observed. C18Al was dissolved at 130 °C for 2 hours and then the solution was cooled to room temperature. The measurements were performed after 1 day aging at the room temperature. Sample solutions independently prepared by the same condition were used at each measurement.

Viscoelastic properties of the samples were measured with Anton Paar MCR300 rheometer. A cone-plate geometry with 50 mm diameter and 3° cone-angle was used. Dynamic mechanical analysis in linear region was carried out in a temperature range of 15 to 75 °C with 10 °C increment. XRD measurements were performed with Rigaku RINT2100H/KLC diffractometer using Ni-filtered Cu Kα radiation. Local structure for both C18Al powder and C18Al/decalin solution were examined at room temperature.

SANS measurements were performed by SANS-U spectrometer at the Neutron Scattering Laboratory of the ISSP, The University of Tokyo, established at C1-2 beam line of JRR3M in JAERI (Tokai), Ibaraki, Japan. The wavelength λ and beam size of incident neutrons was 0.7 nm and 3 mmφ, respectively. The sample to detector distance was changed as 1, 4, and 8 m. A screw type sealing cell (sample volume ca. 0.1 ml) with quartz window was used. Measurements were carried out at room temperature (ca 27 °C), 35, 45, 55 and 65 °C. Circularly averaged intensity I(q) was obtained as a function of the magnitude of wave vector q, defined by q = 4πsin(θ/2)/λ, where θ is scattering angle. The data were corrected for the incoherent scattering of the solvent and the empty cell. The SANS measurement was also performed for C18AI powder at room temperature.

3. RESULTS AND DISCUSSIONS

Figure 1 shows double logarithmic plots of storage modulus, G' and loss modulus, G'' vs. frequency, ω at different temperatures, T. At each temperature, terminal and plateau region behaviors quite resembling to type II micelle of CTAB/NaSal systems are observed. From these data, zero shear viscosity, η₀ and plateau modulus, Gₚ are obtained. Figure 2 shows semi-logarithmic plots of η₀ and Gₚ vs. T. Here, Gₚ value is simply determined as the value at the frequency where the minimum of G'' is located (ωₐ₀ = 90 rad/s, see Figure 3). The values of log η₀ linearly decrease with increase.

Fig. 1. Double logarithmic plots of G' and G'' vs. ω for C18Al/decalin 7 wt% solution at different temperatures. The data at each temperature is vertically shifted to avoid overlapping.
of \( T \), implying that the temperature dependence of \( \eta^0 \) can be expressed by an Arrhenius type equation. The values of \( G_N \) gradually increase with increase of \( T \).

From the interpolation of the data shown in Figure 2, \( \eta^0 \) at 20, 30 and 50 °C are estimated and specific viscosity \( \eta_{sp} \) at these temperatures are obtained by using reported values of solvent viscosity \( \eta_s \) (2.40 cP at 20 °C, 1.76 cP at 30 °C, and 1.58 cP at 20 °C). The \( \eta_{sp} \) values thus obtained are almost constant, irrespective of the \( T \) (2.2 \times 10^4 at 20 and 50 °C, and 2.4 \times 10^4 at 30 °C). Therefore, \( T \) dependence of \( \eta^0 \) can be attributed to the change in \( \eta_s \). \( G_N \) values reduced by the absolute temperature ranged from 0.34 (at 15 °C) to 0.38 (at 75 °C). The remaining difference of these values can be accounted by the temperature dependence of solution density.

By using horizontal shift factor \( a_T \) and vertical shift factor \( b_T \), which reflect the temperature dependence of \( \eta^0 \) and \( G_N \), respectively, master curves of \( G' \) and \( G'' \) are generated as shown in Figure 3. To clearly show the minor difference of \( G'' \) at high frequencies in temperature ranges above and below 55 °C, the master curves are shown in two different \( T \) ranges. Note that the data at 55 °C are included in both the curves. It is clear that the data can be well superimposed with each other in the higher \( T \) range, while the minimum of \( G'' \) become shallower with decrease of temperature in the lower \( T \) range, though their position is unchanged. Neglecting this minor difference in the behavior of \( G'' \), we can conclude that there is no practical difference in the network structure of micelles at different temperatures and the main relaxation process of the system is quite similar to the entangled polymer systems. It is known that minimum of \( G'' \) becomes shallower when molecular weight distribution (MWD) of the sample is broader\(^{12} \).

Therefore, above difference in the behavior of \( G'' \) at high and low temperatures may imply that distribution of the length of micelles become slightly narrower at higher temperature.

Figure 4 shows double logarithmic plots of \( I(q) \) vs. \( q \) at different temperatures. The data at high \( q \) are almost the same irrespective of temperature and show a small shoulder at around \( q = 1 \text{ nm}^{-1} \) while the data at low \( q \) show steep decrease with increase of \( q \). The data at low \( q \) become slightly lower with increase of temperature, though the shape of \( I(q) \) vs. \( q \) curves are almost the same, except the data at 65 °C. At this
$T$, evaporation of solvent from sample cell occurred (probably due to relatively small sample volume and longer measuring time) and a bubble was seen in the cell after the measurement. Therefore, the data at $65^\circ C$ are not reliable. However, since the scattering data still resembles to others and viscoelastic data do not change at higher $T$ range (55 to $75^\circ C$), we speculate that the structure at higher $T$ is the same as that at $55^\circ C$.

Figure 5 compares the small shoulder observed in Figure 4 with SANS and XRD data for C18Al powder. The SANS and XRD data show a narrow peak at around $q = 1.3$ nm$^{-1}$ (corresponds to length of ca 4.8 nm), which is consistent with long period of C18Al crystalline estimated from its structure; two C18 chains extended in the opposite direction on a straight line and another one bent to be parallel with others (trans-zigzag C18 chain : 2.2 nm, Al$^{3+}$ diameter: 0.1 nm).

The shoulder observed for C18Al/decalin is located at slightly lower $q$, implying that the structural unit of micelle is different from crystalline structure.

Figure 6 show cross-sectional Guinier plot for the data shown in Figure 4. There is no practical difference for the values of cross-sectional radius of gyration obtained at different $T$. By using the average value (6.5 nm), theoretical scattering intensity for cylinder is calculated as shown by a solid line in Figure 4. The data and the solid line coincide well at low $q$, confirming that this system has cylindrical structure, though the further details of the structure cannot be elucidated from these data.

From above viscoelastic and structural examinations, we conclude that as long as the sample preparation condition is maintained the same, the network structure of C18Al/decalin micelle is practically the same at different temperatures and the main relaxation process of the network is similar to entangled polymers, at least for limited conditions tested in this study.

**Aknowlegement**

This work was partly supported by the Grant-in-aid for Scientific Research from Ministry of Education, Cultures, Sports, Science and Technology, JAPAN (No. 108550197). SANS measurement was carried out as a joint research of the Institute for Solid State Physics, the University of Tokyo (Proposal No.5557).

**REFERENCES**