

One Remark on the Temperature Dependence of Shear Viscosity in Biphase Region for Cellulosic Lyotropic Liquid Crystals

INTRODUCTION

In previous papers,^{1,2} we reported that the shear viscosity for cellulosic liquid crystalline solutions (LCSs) exhibited a minimum and a maximum with respect to temperature; the anomalous viscometric behavior corresponded to the phase transformation from a liquid crystalline to an isotropic phase through the biphase region in which the isotropic and liquid crystalline phases coexist. In that biphase region, the shear viscosity for LCS increased with increasing temperature. This anomaly is due to varying the volume of the liquid crystalline domain (LCD).³ Therefore, it is helpful to investigate how the volume of the LCD in that region varies with temperature for understanding the temperature dependence of the shear viscosity for the LPSs.

Ciferri et al.⁴ have determined the volume of the LCD as a function of total polymer concentration by means of a centrifugation process at a room temperature. However, it is difficult to determine experimentally the volume of the LCD as a function of temperature by using such a centrifugation process, because the temperature control of a centrifuge can be not so easy as expected and the volume of the LCD is so sensitive to the temperature change.

In this note, we present phenomenological models which account the anomalous viscometric behavior in the biphase region in terms of varying volume of the LCD and compare the shear viscosity observed with that predicted from the models presented.

MODELS

A tentative picture of the anomalous viscometric behavior as a function of temperature is schematically presented in Figure 1; the logarithm of viscosity is plotted against the reciprocal of absolute temperature. The LCDs of hydroxypropyl cellulose^{1,2} and ethyl cellulose⁵ in water and many organic solvents exhibited the similar behavior to that of Figure 1. The plots are linear for a single phase region (isotropic or liquid crystalline) and can be expressed by an equation of the Arrhenius form, but are not for the biphase region. From the point of view of phase transformation, Figure 1 shows that the isotropic phase begins to form at T_2 and the isotropization completely ends at T_1 ; in other words, the volume of the LCD begins to decrease at T_2 , decreases with increasing temperature, and finally becomes to zero at T_1 . Now we assume that the linear relation for the single liquid crystalline and isotropic phases can be extended over a wider range of temperature than the range obtained experimentally when the phase transformation does not occur. The extended linear relations are indicated by the dashed curves in Figure 1. Here we also assume the following mechanical models developed by Takayanagi^{6,7} as shown in Figure 2. Elements in (A) and (B) form the biphase series and parallel models, and the combination shown in (C) and (D) represent two other models. The viscosity in the biphase region is represented by the following equations respectively:

$$\text{model (A): } \frac{1}{\eta_{\text{est}}} = \frac{1 - \psi}{\eta_{\text{iso}}} + \frac{\psi}{\eta_{\text{ani}}} \quad (1a)$$

$$\text{model (B): } \eta_{\text{est}} = (1 - \lambda) \cdot \eta_{\text{iso}} + \lambda \cdot \eta_{\text{ani}} \quad (1b)$$

$$\text{model (C): } \frac{1}{\eta_{\text{est}}} = \frac{\psi}{\lambda \cdot \eta_{\text{ani}} + (1 - \lambda) \cdot \eta_{\text{iso}}} + \frac{1 - \psi}{\eta_{\text{iso}}} \quad (1c)$$

$$\text{model (D): } \eta_{\text{est}} = (1 - \lambda) \cdot \eta_{\text{ani}} + \lambda \left(\frac{\psi}{\eta_{\text{ani}}} + \frac{1 - \psi}{\eta_{\text{iso}}} \right)^{-1} \quad (1d)$$

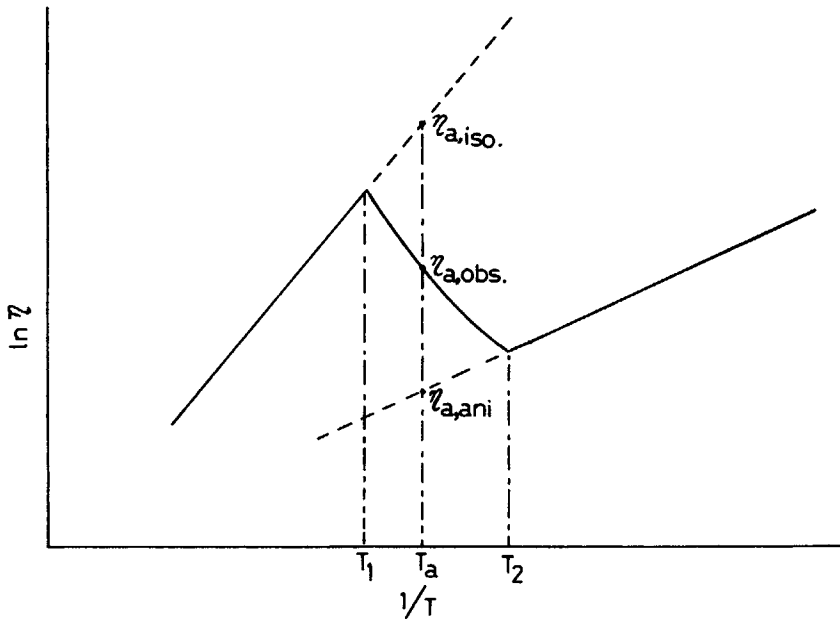


Fig. 1. Schematic picture of temperature dependence of viscosity for liquid crystalline solutions.

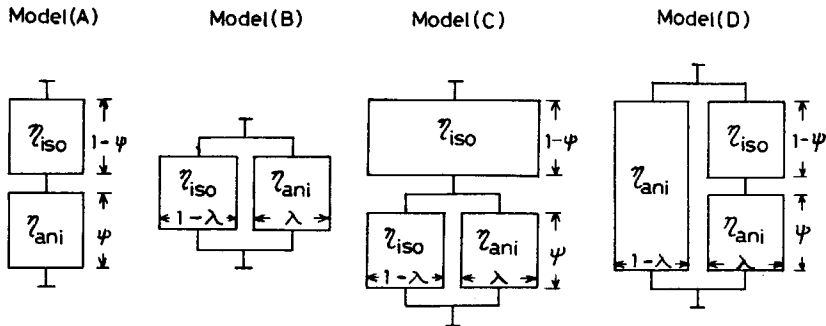


Fig. 2. Mechanical models developed by Takayanagi. See text for explanation of each parameter.

where η_{est} is the viscosity estimated in the biphasic region and η_{iso} and η_{ani} are the viscosities of the isotropic and liquid crystalline phases which are estimated from the dashed curves in Figure 1. λ and ψ are the parameters relating to the mixing state and the composition of the sample solution in the biphasic region; $\lambda \cdot \psi$ is equal to the volume fraction of the LCD, V_{ani} .⁷ We assume the following relation:

$$dV_{ani}/dT = \text{const} \tag{2}$$

Now we can estimate the viscosity in the biphasic region, because the only parameter prescribed to estimate the viscosity is λ , which is chosen arbitrarily as 0.2, 0.4, 0.6, and 0.8. To clarify the description, we explain the estimation procedure of the viscosity. In Figure 1, the viscosities estimated are $\eta_{a,iso}$ and $\eta_{a,ani}$ at T_a , and the viscosity observed is $\eta_{a,obs}$. T_1 and T_2 are specific at a given polymer concentration and shear rate, and ΔT is given. Therefore, from eq. (2) V_{ani} can be obtained; ψ is also obtained when λ is chosen arbitrarily. Then the viscosity at T_a can be estimated from eqs. (1). After the same manner, the viscosity can be estimated at given temperatures.

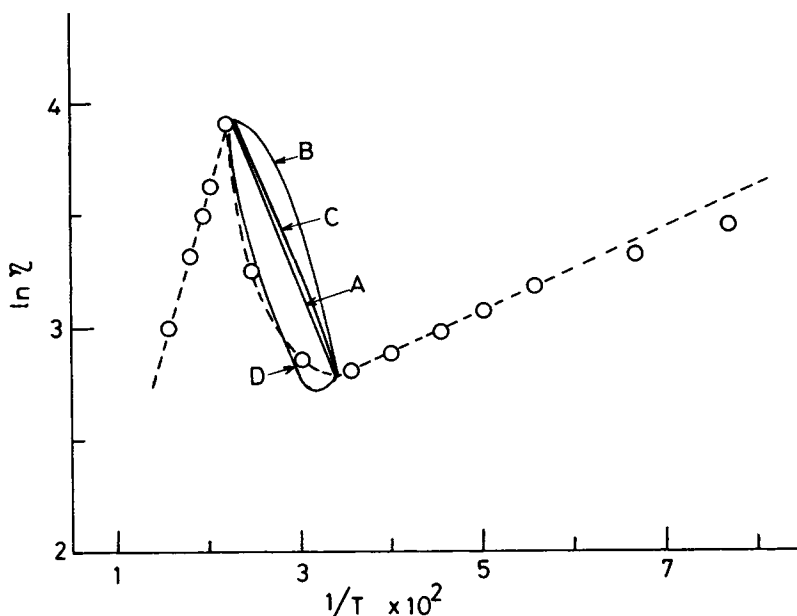


Fig. 3. Temperature dependence of viscosity for 33 wt % solution of ethyl cellulose in *m*-cresol: (---) observed; (—) estimated. Model number corresponds to that in Figure 2; for models (C) and (D) assumed value of λ is 0.8.

In our models, the effect of the domain size on the viscometric behavior in the biphasic region was not considered, particularly because the change of the domain size with temperature seemed to be negligible in comparison with the change of that with shear rate. Further, even if at so a high shear rate that the domain size can be greatly varied, the effect of the domain size on the viscosity in the biphasic region should be involved in the slope of the Arrhenius type curve for the single liquid crystalline phase; the slope, that is, the activation energy for flow, should be dependent on the domain size.

The effects of the specific interactions between polymer and solvent or between polymers, and of molecular weight on the viscosity were also not considered in our models.

EXPERIMENTAL

Commercial reagent grade ethyl cellulose (EC, Tokyo Kasei Kogyo Ltd.) was used. The number-average molecular weight was 1.8×10^4 .⁸ EC powder was dried *in vacuo* at 60°C for 24 h before use. Reagent grade *m*-cresol (Wako Pure Chemical Ind., Ltd.) was used without further purification. Preparation of concentrated solutions and viscometry were given elsewhere.^{1,2} We should note the following. The experimental equilibration of the solution in the biphasic region took a considerable period of time. We needed at least 45 min to begin the measurement of the viscosity after the solution reached to a given temperature.

RESULTS AND DISCUSSION

We compare the viscosities observed in the biphasic region with those estimated using eqs. (1) and (2), as shown in Figure 3. The data observed are for 33 wt % solutions of EC in *m*-cresol. Figure 3 clearly shows that model (D) is most preferable to estimating the viscometric behavior in the biphasic region. The relation between the mechanical models and the actual textures of the LCD in the biphasic region is not clear, but according to Takayanagi's concept⁷ the model (D) suggests that the isotropic phase is dispersed heterogeneously in the liquid crystalline phase.

In our procedure of estimating viscosity in the biphasic region, three assumptions were made: (1) extension of the linear relation between log viscosity and $1/T$, (2) mechanical models, and (3)

eq. (2). On the first assumption, we think, there were no serious problems. Regarding the second assumption, many other models can be proposed, for example, the four-element model etc., but basically the three-element model is simple enough to preliminarily investigate the viscometric behavior. However, it is still uncertain as to whether to apply the model to shear viscosity, because Takayanagi's model is for mechanical properties. We should make clearer the physical meanings of our model. Concerning the third assumption, little is known. However, we suppose that the validity of the third assumption would be greatly dependent on the distribution of the molecular weight, and strictly speaking, the third assumption would not be applicable to the viscometric behavior in the vicinity of the maximum and minimum points. Then, we need experimental evidence in confirmation of the third assumption or of the formula alternative to eq. (2).

Finally, it is important to note that the minimum and maximum in the concentration dependence of shear viscosity does not always correspond to the phase transformation and that the concentration dependence of the viscosity in the biphasic region approximately follows the Taylor relation.^{9,10} Therefore, we need to determine carefully the viscometric behavior in the vicinity of the maximum and minimum points, taking into account of the distribution of the molecular weight, and to make quantitatively clearer our model.

CONCLUSIONS

The mechanical models for accounting for an anomalous temperature dependence of shear viscosity in the biphasic region for lyotropic liquid crystals are phenomenologically examined in terms of varying volume of the liquid crystalline domain, with three simplifying assumptions. A three-element model was preferable to estimating the anomaly in the biphasic region, in comparison with the experimental data for the liquid crystalline solution of ethyl cellulose in *m*-cresol. However, we need more data for the viscometric behavior to make our model more meaningful.

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