The Superposition of Viscoelastic Data for Solutions of Carboxymethyl Cellulose

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In a preceding paper,1) the present authors reported that the viscoelastic data of sodium polyacrylate (Na-PAA) solutions could be superposed on a composite curve by a slight modification of the Ferry's method of reduced variables, and that the viscoelasticity of the polyelectrolyte solutions studied showed abnormal behavior in comparison with that of usual polymers. It was considered that the charged groups along the molecular chains diminish intermolecular entanglements by means of electro-repulsive force.

Sodium carboxymethyl cellulose (Na-CMC), which is studied here, has not only electrolytic groups but also hydroxyl groups, which seem to form hydrogen bonds between molecules easily. It may be expected that the superposition of viscoelastic data for Na-CMC solutions will be influenced by this molecular nature.

Na-CMC(D.P.=250, D.S.=0.7, pH=7.0 at 1%), prepared from dissolving pulp in an 88% isopropanol medium by carboxymethylation, was used to study the superposition of frequency and rate of shear-dependent curves of the viscosity and rigidity.

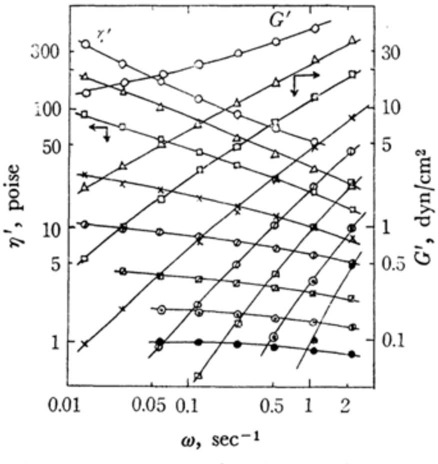

Fig. 1. Dynamic data for 0.9—3 g/100 m*l* carboxymethyl cellulose solutions at 25°C.

○ 3.00 g/100 m*l*, △ 2.66 g/100 m*l*
□ 2.34 g/100 m*l*, × 2.00 g/100 m*l*
⦶ 1.70 g/100 m*l*, ⊠ 1.36 g/100 m*l*
⊙ 1.15 g/100 m*l*, ● 0.92 g/100 m*l*

The dynamic data, shown in Fig. 1 (η': dynamic viscosity, G'; dynamic rigidity, ω; angular frequency), were obtained by means of a torsionally-oscillating rheometer, a "Rheometer Almighty." η' and G' were evaluated from Markovitz's equation.2) The flow data, shown in Fig. 2 (η_a; non-Newtonian viscosity, γ_a; rate of shear), were obtained with the same apparatus by the steady revolution of the outer cylinder, while η_a was evaluated under the assumption of a Newtonian flow.

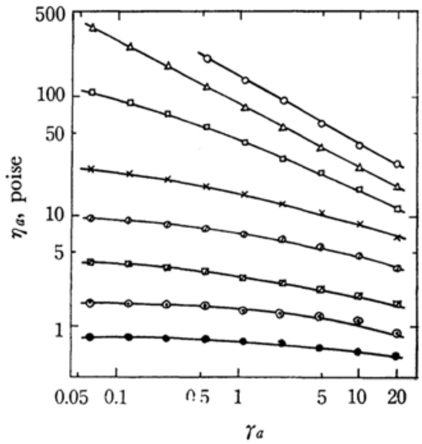

Fig. 2. Flow data for 0.9—3 g/100 m*l* carboxymethyl cellulose solutions at 25°C.

For the reduction of data to the reference concentration, C_0 (=2 g/100 m*l*), at a constant temperature, the following reduced variables were assumed:

$$G_r' = G'\cdot F(C_0/C) \tag{1}$$

$$\eta_r' = \eta'\cdot\eta_0/\eta \tag{2}$$

$$\omega_r = \omega\cdot a_c \tag{3}$$

$$\eta_{ar} = \eta_a\cdot\eta_0/\eta \tag{4}$$

$$\dot{\gamma}_{ar} = \dot{\gamma}_a\cdot a_c \tag{5}$$

$$a_c = F(C_0/C)\cdot\eta/\eta_0 \tag{6}$$

F means a function of the concentration, η is the zero shear viscosity, and C is the concentration. The suffix 0 indicates the value at the reference concentration, C_0. In Ferry's reduced variables $F(C_0/C)$ is equal to C_0/C itself.3)

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1) S. Kuroiwa and M. Nakamura, This Bulletin, **39**, 1602 (1966).

2) H. Markovitz, *J. Appl. Phys.*, **23**, 1070 (1952).

3) J. D. Ferry, *J. Am. Chem. Soc.*, **72**, 3746 (1950).

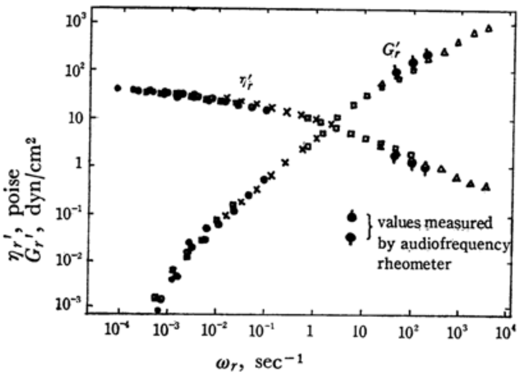

Fig. 3. Composite curves at 2 g/100 m*l*, 25°C of carboxymethyl cellulose solutions in Fig. 1.

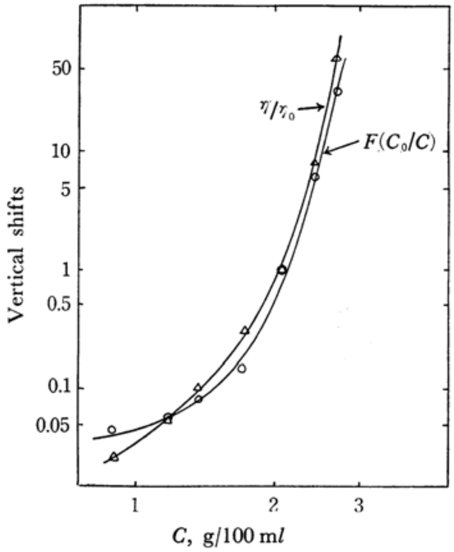

Fig. 4. Vertical shift for superposition of the dynamic data in Fig. 1.

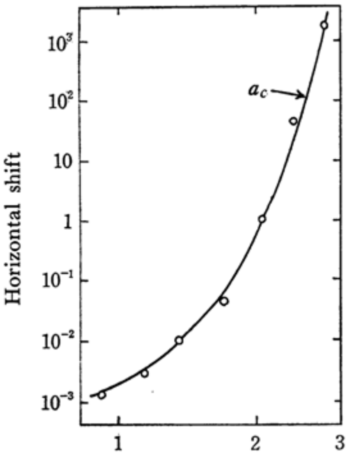

Fig. 5. Horizontal shift for superposition of the dynamic data in Fig. 1.

The vertical and horizontal shifts of the log-G'-log ω and log η'-log ω curves resulted in the composite curves shown at $C_0=2$ g/100 m*l* in Fig. 3. The vertical and horizontal shifts, $F(C_0/C)$ and a_c were both functions of C as illustrated in Figs. 4 and 5 respectively.

The composite curve, log η_{ar}-log γ_{ar} in Fig. 6 is composed of the vertical and horizontal shifts of viscosity curves caused by the shift factors shown in Figs. 4 and 5.

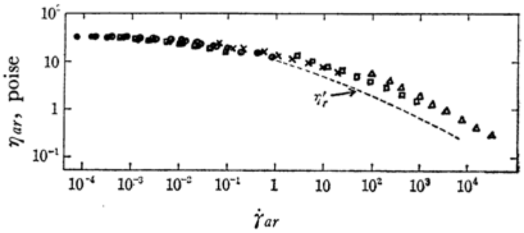

Fig. 6. Composite curve at 2 g/100 m*l*, 25°C of carboxymethyl cellulose solutions in Fig. 2.

To check the validity of the results of superposition shown in Fig. 3, η' and G' at $C=C_0$, as measured by a rheometer for the audiofrequency range, are plotted in the same figure.

Regarding the results of superposition, the following may be pointed out: (1) The graphical superposition of the viscoelastic data of Na-CMC solutions at various concentrations seems to be possible, though the theoretical meanings are not clear.

(2) The shift factors for the horizontal shift

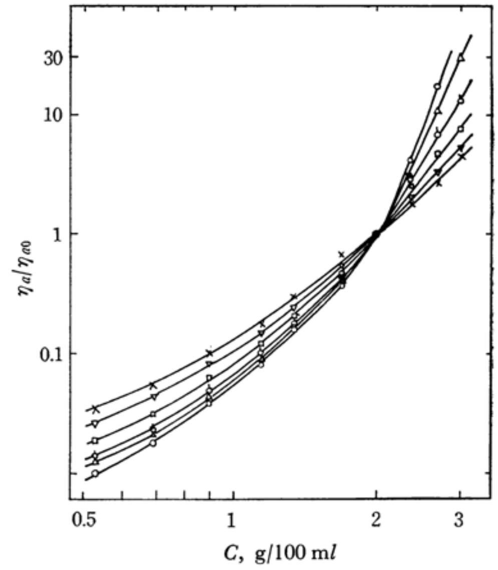

Fig. 7. Concentration dependence of non-Newtonian viscosity at various sheaving rates.

○ $\dot{\gamma}_a=0.062$, △ $\dot{\gamma}_a=0.185$
○ $\dot{\gamma}_a=0.500$, □ $\dot{\gamma}_a=2.000$
▽ $\dot{\gamma}_a=8.000$, × $\dot{\gamma}_a=23.50$

along the log ω axis of the log G'-log ω and log η'-log ω curves are identical in the two cases. This phenomenon may be interpreted by assuming that all the relaxation times involved are multiplied by the shift factor, $a_c(=F(C_0/C)\cdot\eta/\eta_0)$, when the concentration varies from C_0 to C. This assumption is the one used previously in Ferry's method of reduced variables.

(3) However, $F(C_0/C)$, the vertical shift of the log G'-log ω curves, increases with an increase of C, as may be seen in Fig. 4. This is completely incompatible with Ferry's reduced variables. The reason for this is obscure.

(4) In the nearly-straight portions of the log-η/η_0 - log C curves in Fig. 4, η/η_0 is approximately proportional to C^{14-15}. This high dependence of the zero-shear viscosity on the concentration obtained by the procedure of graphical superposition was checked qualitatively as follows. α, the slope of the nearly-straight portion in the log η_a/η_{a0} - log C curves in Fig. 7 was plotted against $\dot{\gamma}_a$ in Fig. 8. In this figure, α seems, as expected, to have a value larger than about 14—15 when $\dot{\gamma}$ approaches small values; $\lim_{\dot{\gamma}_a\to 0}\eta_a/\eta_{a0}=\eta/\eta_0$ is also assumed, as in the usual definition.

For the usual concentrated polymer solutions, the $\eta/\eta_0 \propto C^{5-6}$ relation has been known.[4-8] In the concentrated solutions of Na-PAA, η/η_0 is proportional to C^2.[1] This extremely small dependence of the zero-shear viscosity on the concentration for the Na-PAA solutions may be attributed to the intermolecular repulsion caused by the charged carboxyl groups. On the other hand, for Na-CMC solutions, it may be considered that the strong tendency toward intermolecular association by hydroxyl groups surpass the repulsive effect by the carboxyl groups and the extremely large dependence of η/η_0 on the concentration results.

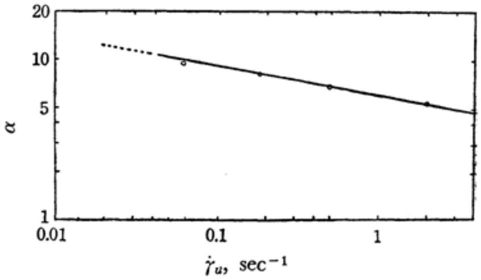

Fig. 8. Shearing rate dependence of slope α in straight portions ($C>2$) of curves in Fig. 7.

(5) The log η_a-log $\dot{\gamma}_a$ curves and log η'-log ω curves are both reduced to a composite curve by the same shift factor as hold in the case of Na-PAA solutions. The similarity between η'-ω-C and η_a-$\dot{\gamma}_a$-C relations for these rheologically-peculiar substances seems to suggest the mechanism of non-Newtonian viscosity and its relation to the dynamic viscosity.

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7) D. J. Plazek and J. D. Ferry, *ibid.*, **8**, 592 (1953).

8) E. Fukada and M. Date, *Kobunshi*, **11**, 1284 (1964).