Some Rheological Properties of Sodium Polyacrylate Solutions

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(Received October 20, 1965)

The viscoelastic properties of aqueous solutions of sodium polyacrylate (degree of polymerization=45000) were studied. It seems that the results described below reveal some characteristics of the polyelectrolyte studied.

The dynamic rigidity and viscosity (G', η') and the steady flow viscosity (η_a) were measured by a coaxial double cylinder rheometer,[*1] in which the outer cylinder was driven to oscillate or revolve. G' and η' were calculated by the method described by Markovitz.[1] η_a is the apparent viscosity, assuming the Newtonian flow.

For a comparison of G' with the rigidity G, calculated from the elastic recovery following a steady flow,[*2] the data reported in a previous paper were used.[2]

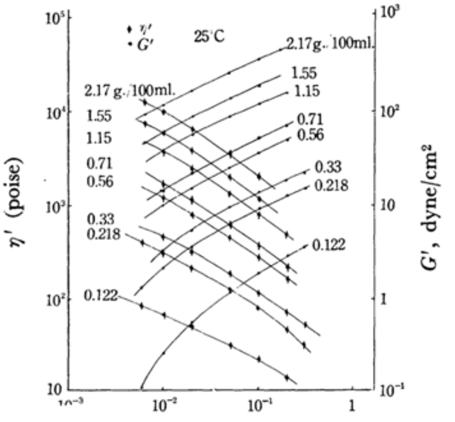

Fig. 1. Dependence of η' and G' on ω and concentration.

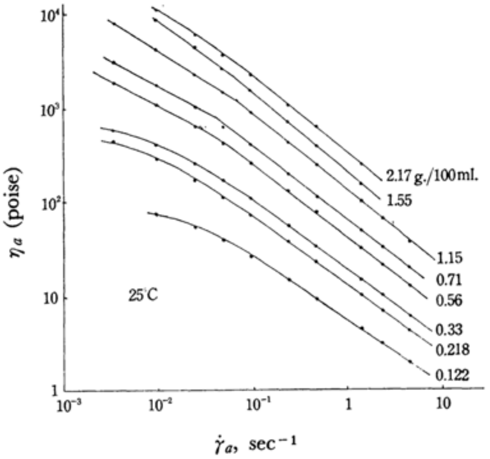

Fig. 2. Dependence of η_a on $\dot{\gamma}_a$ and concentration.

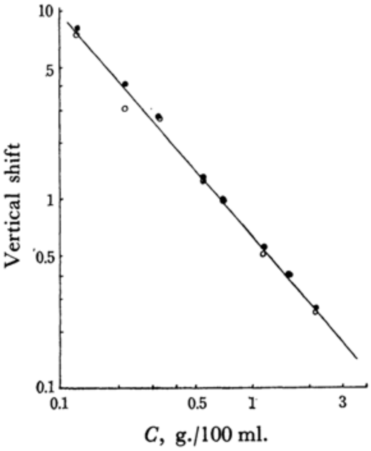

Fig. 3. Relation between vertical shift and concentration for the superposition of $\log G'$ vs. ω plotts.

○ Graphical procedure

● $(C_0/C)^{1.2}$ (calc. value)

The experimental results are illustrated in Figs. 1 and 2. In Fig. 1, the vertical shifts along the $\log G'$ axis for the superposition of $\log G' - \log \omega$ curves of varied concentrations were not proportional to (C_0/C), but to $(C_0/C)^{1.2}$, as may be seen in Fig. 3. C is the concentration, and the subscript refers to the reference concentration. Therefore, Ferry's reduced variables,[3] G_r', η_r' and ω_r, for the concentration were modified as follows at a costant temperature:

$$G'_r = G'(C_0/C)^{1.2} \tag{1}$$

$$\eta'_r = \eta'(\eta_0/\eta) \tag{2}$$

$$\omega_r = \omega(\eta/\eta_0)(C_0/C)^{1.2} \tag{3}$$

η indicates the zero shear viscosity. η/η_0 as a

[*1] Rheometer Almighty, manufactured by the Iwamoto Seisakusho Co. Ltd.

[*2] Appendix

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

2) S. Kuroiwa and M. Nakamura, *Chem. High Polymer*, **22**, 385 (1965).

3) J. D. Ferry, *J. Am. Chem. Soc.*, **72**, 1102 (1950).

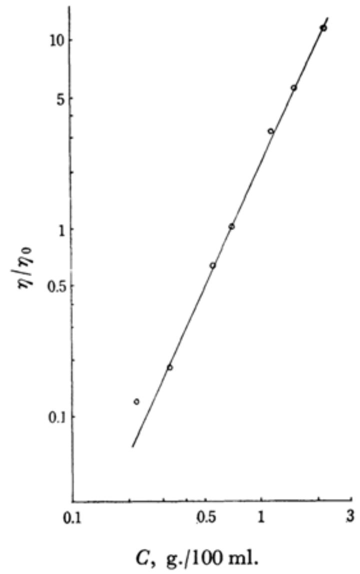

Fig. 4. Relation between η/η_0 and concentration.

function of C was determined from $(C_0/C)^{1.2}$ and the horizontal shifts along the log ω axis by means of Eq. 3. A linear relation between log η/η_0 and log C was obtained, as is illustrated in Fig. 4.

Reduced variables for η_a and $\dot{\gamma}_a$ (the average shearing rate) were defined as:

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

$$\dot{\gamma}_{ar} = \dot{\gamma}_a(\eta/\eta_0)(C_0/C)^{1.2} \tag{5}$$

Master curves reduced to 0.71 g./100 ml. are represented by Figs. 5 and 6. In Fig. 6, η_{ar} shows a small fluctuation, but it seems to be within the range of experimental error. It may be observed in Fig. 6 the difference between η_{ar} and η'_r becomes obvious with an increase in $\dot{\gamma}_{ar}$ or ω_r, as have been described by several authors for various polymer systems.[4-8] However, the concentration dependence of the zero shear viscosity seems to be very small compared with that of usual polymers, i e. $\eta/\eta_0 \propto C^2$. In the concentration range (0.25—1.5 g./100 ml.) studied, products of the chain length, Z, and the volume fraction of the solute, v, were calculated as 230—1400. The critical value of Zv, i. e., $Z_c v_c$, is known to be about 200—1400 in usual polymers.[9] The $Z_c v_c$ value for aqueous solutions of polyacrylic acid had been reported as 130.[10] Further, the η of the sample may be expected from Fig. 2 to be larger than 10^2 poise. Usually, under such conditions, the η values of many polymer solutions depend on C^{5-6}.[7,11-14] For example, Fukada reported that the η/η_0 values of aqueous collagen solutions in a concentration range similar to that of this study depend on C^6,

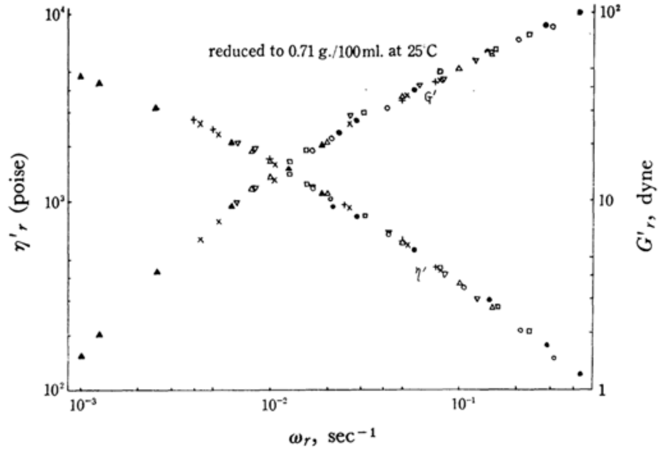

Fig. 5. Results of superposition, using modified shift factors.

● 2.17 g./100 ml. ○ 1.55 g./100 ml.
□ 1.15 g./100 ml. △ 0.71 g./100 ml.
▽ 0.56 g./100 ml. × 0.33 g./100 ml.
+ 0.218 g./100 ml. ▲ 0.122 g./100 ml.

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4) T. W. Dewitt, H. Markovitz, E. D. Padden and J. Zapas, *J. Colloid Sci.*, **10**, 174 (1955).

5) H. Markovitz and B. Williamson, *Trans. Soc. Rheol.*, **1**, 25 (1965).

6) W. Philippoff, *J. Appl. Phys.*, **25**, 1102 (1954).

7) S. Onogi, I. Hamana and H. Hirai, ibid., **29**, 1503 (1958).

8) T. Arai, *Chem. High Polymer*, **18**, 292 (1961).

9) T. G. Fox and S. Gratch S. Loshaek, "Rheology, 1," Ed. by Eirich, Acad. Press, New York (1965).

10) J. G. Brodnyan and E. L. Kelly, *Trans. Soc. Rheol.*, **7**, 125 (1963).

11) R. F. Landel, J. W. Berg and J. D. Ferry, *J. Colloid Sci.*, **12**, 400 (1957).

12) J. D. Ferry, ibid., **7**, 498 (1951).

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

14) E. Fukada and M. Data, *Kobunshi*, **11**, 1284 (1964).

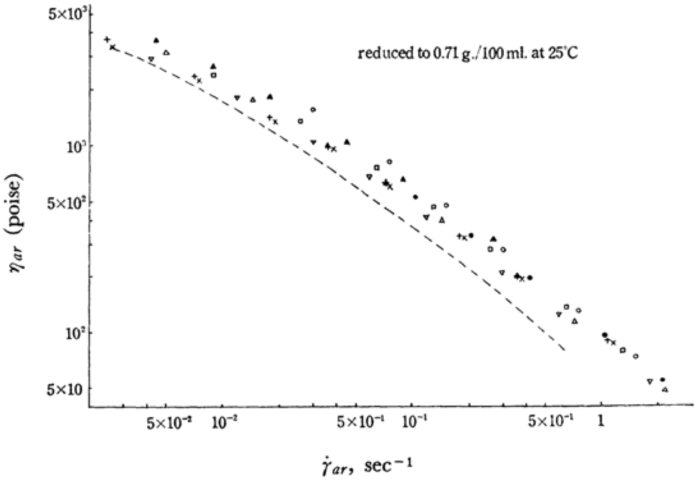

Fig. 6. Result of superposition, using modified shift factors.

●	2.17 g./100 ml.	○	1.55 g./100 ml.
□	1.15 g./100 ml.	△	0.71 g./100 ml.
▽	0.56 g./100 ml.	×	0.33 g./100 ml.
+	0.218 g./100 ml.	▼	0.122 g./100 ml.
----	η'		

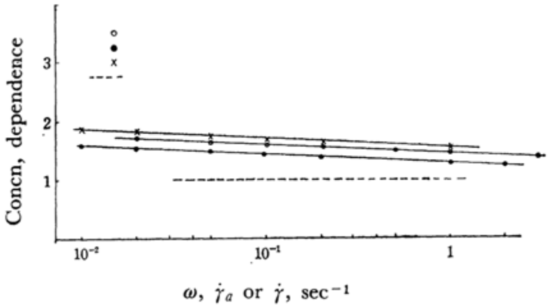

Fig. 7. Variation of concentration dependencies of η', G'. η_a and G with ω, $\dot{\gamma}_a$ and $\dot{\gamma}$, respectively.

○	$\eta_a \sim \dot{\gamma}_a$	●	$\eta' \sim \omega$
×	$G' \sim \omega$	----	$G \sim \dot{\gamma}$

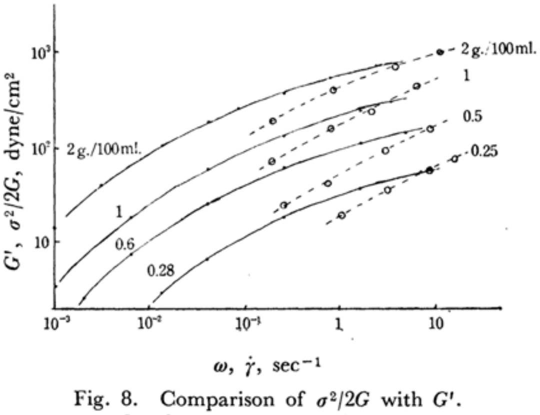

Fig. 8. Comparison of $\sigma^2/2G$ with G'.
● G' ○ $\sigma^2/2G$

where a procedure analogous to that used in this study was employed for evaluating η/η_0.[14]

Accordingly, it may be said that the nature of the molecular interactions of the polyelectrolyte studied here is remarkably different from that of other polymers. In other words, some mechanisms other than the so-called Bueche entanglements[12,15] may dominate the viscosity of the solutions, in spite of their high Zv and η values. The extraordinarily anomalous non-linearity of flow and the very large recoverable strain of the sample[2] can probably be interpreted by means of this abnormal intermolecular mechanism.

When $\log G'$, $\log \eta'$, $\log \eta_a$ and $\log G$ were plotted against $\log C$ at fixed ω, $\dot{\gamma}_a$ and $\dot{\gamma}$ (true shearing rate) values respectively, straight lines were obtained. The slopes of these lines were estimated; they are plotted against ω, $\dot{\gamma}_a$ and $\dot{\gamma}$ respectively in Fig. 7. In this figure the concentration dependence of η_a seems to be extrapolated to about 2, whereupon $\dot{\gamma}_a$ becomes small. This is in agreement with the relation, $\eta/\eta_0 \propto C^2$, described above.

In Fig. 8, $\log G'$ is compared with $\log(\sigma^2/2G)$, where ω and $\dot{\gamma}$ are assumed to be equivalent. σ is the shearing stress. $\sigma^2/2G$ may be equal to $(P_{11}-P_{22})/2$, in which $P_{11}-P_{22}$ is the normal stress in rheogoniometry. According to the theory of Coleman et al.,[16] $(P_{11}-P_{22})/2$ as a function of the shearing rate must approach G' as a function of ω, when shearing rate of ω becomes small. This theory was confirmed by Kotaka et al. to hold for polystyrene solutions.[17] In Fig. 8, however, there

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[15] F. Bueche, *J. Chem. Phys.*, **22**, 603 (1954).

[16] B. D. Coleman and H. Markovitz, *J. Appl. Phys.*, **35**, 1 (1954).

[17] T. Kotaka and K. Osaki, *Bull. Insi. Chem. Res. Kyoto Univ.*, **39**, 331 (1962).

seems to be no tendency for G' and $\sigma^2/2G$ to approach each other when ω or $\dot{\gamma}$ becomes small. The reason for this is not clear. However, it is not inconceivable that the discrepancy between the theoretical and the experimental results comes from some thixotropic characteristic of the substance.

Appendix

$$G=\sigma_i S_i = \sigma_i \bigg/ \left\{ \frac{2n\theta_e}{1+(R_i/R_0)^{2n}} \right\}$$

S_i; Recoverable strain at the inner cylinder surface
θ_e; Angular displacement of the inner cylinder following steady flow
σ_i; Shearing stress at the inner cylinder surface
R_i; Inner cylinder radius
R_0; Outer cylinder radius
n; Slope of the $\log \theta_e$ - $\log \sigma_i$ plot