Rheological Properties of Hydrogels of Agar-agar

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Hydrogels of agar-agar are typical examples of polymeric thermo-reversible gels, and have long been the objects of the researches in colloid chemistry for these several decades[1]. Much remains unknown, however, concerning these gels even at present. In the study of thermo-reversible gels rheological methods are the most appropriate ones, and especially, the recent development of rheology has brought to light many new means for that purpose. The author has made a series of rheological studies on thermo-reversible gels[2,3], and a stress relaxation experiment has been made on the hydrogels of agar-agar, a part of the result of which was reported previously[2]. In this paper more comprehensive results and discussion are given.

Experimental

Sample. — Sample I was given by Nihon Kaiso Kogyo Co., whose specification is shown in Table I together with that of sample II used in the previous experiment[2] for comparison. The intrinsic viscosity $[\eta]_{25}$ at 25°C of the aqueous solution of agar-agar was obtained by means of a capillary viscometer of the Ostwald type, and the molecular weight was calculated from the value of the intrinsic viscosity according to the following formula 1[4].

$$[\eta]_{25}=(3.7\times10^{-4})M_v \qquad (1)$$

The obtained molecular weight is, however, an approximate one, because the reproducibility in the viscosity measurement at 25°C is not so good as that in the measurement at 60°C described below. The preparation of cylindrical gels for the stress relaxation experiment was made as follows. A powder sample was mixed with water in a vessel, and was dissolved by heating on an oil bath with a reflux condenser for two hours, and then was poured into cylindrical moulds. After the surfaces of the cylinders were covered with liquid paraffin in order to avoid the evaporation of water, the specimens were annealed in a thermostat. After 24 hr. specimen gels were taken out from the moulds and were aged at room temperature for more than two weeks. The dimension of the specimen was about 3 cm. in height and 2 cm. in diameter. The preparation of the solution for the measurement of viscosity was made according to the same procedure as that described above, and the measurement was made directly after the preparation.

Apparatus.—A chainomatic relaxometer was used to measure the relaxation of Young's modulus of the cylindrical gels, which was the same one as that used previously[2,3].

TABLE I. SAMPLES

	Sample I	Sample II
Ashes, %	2.9	1.5
$[\eta]_{25}$, 100 cc./g.	16.1	2.9
Molecular weight	40000	8000

Results and Discussion

Viscosity of Agar-agar Solution. — The data of viscosity for the solution of sample I at 60°C are given in Fig. 1. As is seen in Fig. 1, the curve of η_{sp}/C vs. C relation rises with decrease of concentration after passing through a minimum point. This is the characteristic of the solution of polyelectrolyte in general and the same behavior of solutions of agar-agar was reported recently by Sakamoto and Kishimoto[5].

Stress Strain Relation. — The setress σ of 2.6% gel of sample I at 25°C is plotted against the compressional strain γ in Fig. 2. The stress σ was measured accurately 2 min. after the instant of loading for all strains. It is

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[1] T. Nakagawa, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*) **72**, 390, 626 (1951), F. Hirata, ibid., **58**, 1156 (1937); **59**, 1, 7 (1938); N. Hirai, ibid., **72**, 837 (1951); **73**, 65, 68 (1952); K. Ninomiya, ibid., **76**, 72 (1955).

[2] K. Arakawa and K. Atsumi, ibid., **80**, 133 (1959).

[3] K. Arakawa, This Bulletin, **31**, 842 (1958); **32**, 1248 (1959); **33**, 1568 (1960).

[4] N. Hirai and N. Nishimura, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **75**, 248 (1954).

[5] M. Sakamoto and A. Kishimoto, *Bull. Japan. Soc. Sci. Fisheries*, **26**, 25 (1960).

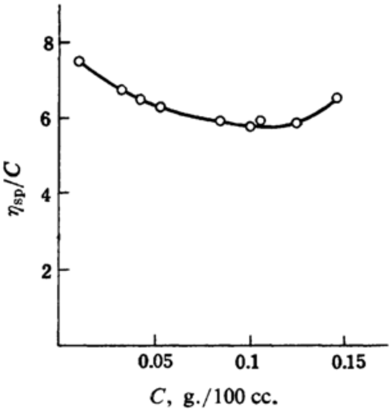

Fig. 1. Viscosity vs. C relation.

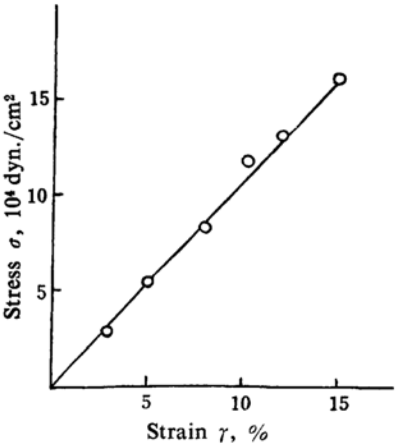

Fig. 2. Stress strain curve at 25°C.

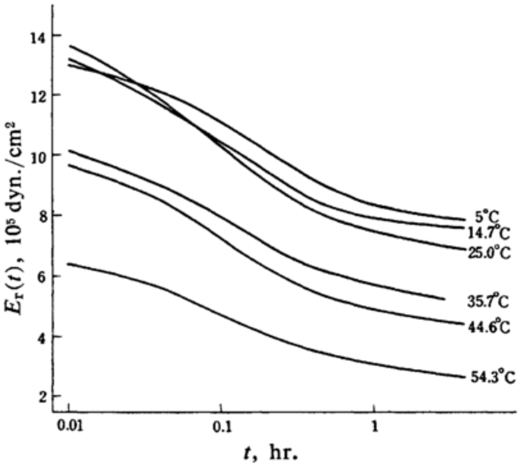

Fig. 3. Relaxation Young's modulus of 2.6% gel (sample I).

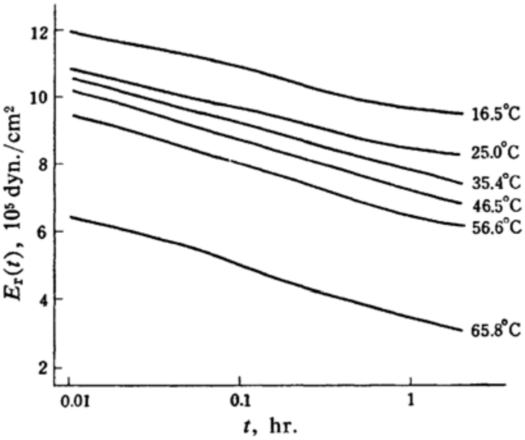

Fig. 4. Relaxation Young's modulus of 2.6% gel (sample II).

clearly seen in Fig. 2 that the stress strain relation is linear within the amount of strain, 15%.

Stress Relaxation. — The relaxation Young's modulus $E_r(t)$ of 2.6% gel of sample I under constant strain at various temperatures is plotted against $\log t$ in Fig. 3, where t is time and $E_r(t)$ is σ/γ. The amount of the imposed strain γ is 5% for all temperatures, which is within the range of the linear relation between stress and strain.

The data of stress relaxation on the hydrogel of sample II of the same concentration, which were reported previously[2], are plotted again in Fig. 4 for comparison, but without the multiplication factor $298/T$ in this case. The relaxation curves in Fig. 3 show the inversion of the mutual position with lapse of time. It may be said that in the short time region and at the comparatively low temperature rubber elasticity appears predominantly, but with the lapse of time the junction cleavage occurs more frequently at the higher temperatures. However, in Fig. 4 no inversion is seen. This may be partly attributed to the difference in the molecular weight of agar-agar.

Analysis of Relaxation Data by Mechanical Model. — The mechanical behavior of these gels is represented by the 6-elements mechanical model shown in Fig. 5. According to this model, $E_r(t)$ under constant strain is expressed by Eq. 2,

$$E_r(t)=E_1e^{-t/\tau_1}+E_2e^{-t/\tau_2}+E_3e^{-t/\tau_3} \qquad (2)$$

where $\tau_1=\eta_1/E_1$, $\tau_2=\eta_2/E_2$, and $\tau_3=\eta_3/E_3$.

The results obtained from the curves in Fig. 3 and Fig. 4 by means of Eq. 2 are given in Table II. The calculation of the model constants was made by repeating the procedure described in the previous paper[2], when the following condition (3) was assumed.

$$\tau_1 \gg \tau_2 \gg \tau_3 \qquad (3)$$

As seen in Table II, this is satisfied.

The Maxwellian element of the relaxation time τ_1 may be regarded as the representation

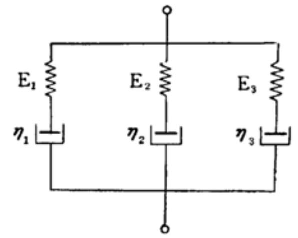

Fig. 5. Mechanical model.

TABLE II. CONSTANTS OF MECHANICAL MODEL OF 2.6% GEL

Sample I °C	E_1 10^5 dyn./cm^2	E_2	E_3	τ_1 hr.	τ_2 min.	τ_3 min.
5	8.2	4.3	1.5	90	16	1
14.7	8.0	4.3	2.2	90	12	1
25.0	7.8	4.2	3.0	40	11	1
35.7	5.8	2.8	2.9	34	17	3.5
44.6	5.0	2.5	3.5	26	18	3.8
54.3	3.2	1.5	2.2	13	18	3.8
Sample II						
16.5	10.0	1.5	1.5	42	12	1
25.0	8.8	1.6	1.6	42	13	0.8
35.4	8.4	1.2	1.9	18	17	1.4
46.5	7.9	1.8	1.3	15	10	1
56.6	7.0	1.8	1.2	17	12	0.8
65.8	3.9	1.4	1.7	9.8	17	1.4

of the main network structure. The linkage supporting this network may be of secondary nature, considering that the hydrogel of agar-agar makes sol-gel transition reversible, and the bond cleavage process in the gels under constant strain may occur at the junctions in the network, not along the network chains. From the τ_1 vs. $1/T$ relation shown in Fig. 6, the average activation energy $\Delta\overline{H}$ is obtained for the dotted line, and is given in Table III, together with the values calculated from the previous data[2] for 4.0 and 1.0% gel of sample II.

$$\Delta H = R\frac{\partial \ln \tau_1}{\partial (1/T)} \tag{4}$$

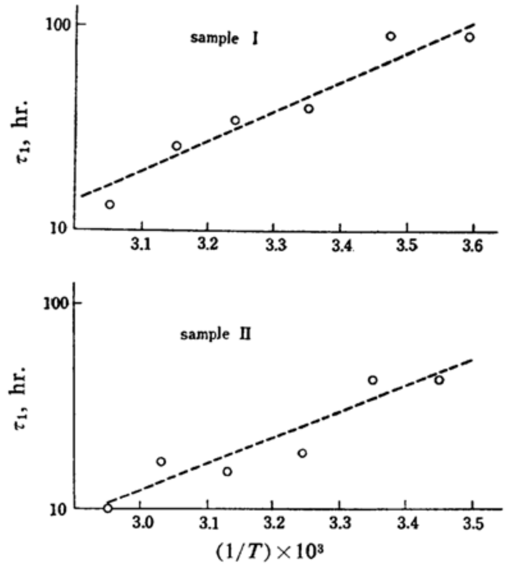

Fig. 6. τ_1 vs. $1/T$ relation of 2.6% gel.

TABLE III. AVERAGE ACTIVATION ENERGY $\Delta\overline{H}$

	Sample I	Sample II		
Concn., %	2.6	1.0	2.6	4.1
$\Delta\overline{H}$, kal./mol.	6.6	4.8	5.8	4.5

In the agar-agar gels the chain skeleton is composed of the chain of galactose. In natural cellulose the activation energy for the cleavage of hydrogen bonds along a-axis in crystalline region is 7~8 kcal./mol.[6] The value given in Table III is 4.5~6.6 kcal./mol., which is smaller than the above value in natural cellulose, and is camparable with the activation energy of the hydrogen bond between water molecules, 4.5 kcal./mol., and that for ethyl alcohol, 6.2 kcal./mol.[7] From the above consideration it may be said that in the hydrogel of agar-agar the secondary bond between each agar-agar molecule which constructs the gel structure is the hydrogen bond between galactose, and that the bond is a little weakened by the effect of solvent molecule, compared with the hydrogen bond in the micelle of natural cellulose.

Summary

A rheological study was made for the hydrogels and the solution of agar-agar. The viscosity vs. concentration relation exhibits the character of polyelectrolyte. From the stress relaxation data obtained by a chainomatic balance relaxometer the following results were obtained.

1) The behavior of hydrogels of agar-agar is represented by the 6-elements mechanical model.

2) The activation energy of the secondary bond between agar-agar molecules which constructs the gel structure is 4.5~6.6 kcal./mol.

Then, there was some discussion on the structure of the hydrogels of agar-agar.

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[6] N. Saito, "High Polymer Physics", Shokabo, Tokyo (1958), p. 8.

[7] L. Pauling, "The Nature of the Chemical Bond", Cornell Univ. Press, Ithaca (1940), Chap. 9.