Electron Microscopic Study on Some Viscous Colloidal Solutions

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The viscous colloidal solutions of organic high polymer give the network or thread-like structures in the electron microscopic image. It seems that the network structure was formed during a drying process of the specimens for electron microscopy and the thread-like structure existed at the highly hydrated state in the sols or gels.

INTRODUCTION

The properties of viscous colloidal solutions and gels have long been interested by colloid chemists. Recently, many studies have been done from the rheological standpoint. The studies of the gel structure by means of electron microscopy have scarcely been made except those of soaps.[1),2)] The authors have observed the interesting figure of mucilage of *Abelmoshus Manihot* by electron microscopy with S. Ikawa.[4)] The present paper provides electron microscopic study on some viscous colloidal solutions.

SAMPLES

The samples produced naturally or synthesized were used as viscous solutions as shown in Table 1. One drop of the sample solution was mounted on a specimen holder for electron microscopy with formvar supporting-film and dried. After shadow-casting the specimen was observed by an electron microscope of the type TRS-50B.

DETERMINATION OF VISCOUS BEHAVIORS

The spinnability was measured as one of the viscous behaviors. A glass rod of 5 mm dia. was dipped 15 mm in the sample solution and drew up at a speed of 10 cm/sec. When a thread cut off, the distance between the tip of the rod and the surface of the solution was defined as the spinnability. The visco-elasticity of the sample solution was also measured by Schwedoff apparatus.[3)]

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RESULTS

The results of these experiments are summarized in Table 1. Some explanations are given as follows.

1. Mucilage of *Abelmoshus Manihot*[4)]

Mucilage of *Abelmoshus Manihot* (Tororoaoi) has been used in making Japanese hand-made paper as "Neri" and the components of it are almost the mixture of carbohydrates. The electron micrograph of mucilage was a typical network as shown in Fig. 1. By heating or exposing to ultrasonic wave the spinnability and the visco-elasticity decreased markedly. An electron micrograph of it heated at 80°C for 2 hours was granular as shown in Fig. 2. The viscous characters after heat treatment or ultrasonic irradiation were not restored to the original state upon standing for many hours at room temperature.

2. Slime of Laminaria

A small quantity of laminaria were soaked in distilled water and kept in a refrigerator for half a month. An electron micrograph of viscous slime is shown in Fig. 3. The spinnability and the viscosity of it were great as described in Table 1, but by heating or ultrasonic irradiation these properties were decreased markedly and the electron micrograph changed to granular form similar to that of mucilage of *Abelmoshus Manihot.*

3. Sodium Polyacrylate

Sodium polyacrylate is also used in making Japanese hand-made paper as a substitute for "Neri". The electron micrograph was a network as shown in Figs. 4 and 5. The thickness of the net increased with the concentration. The electron micrograph and the viscous characters were not changed by heating or ultrasonic irradiation.

4. Cellulose Acetate

Cellulose acetate acetone solution was sampled on a specimen holder with supporting film coated by SiO_2. An electron micrograph is shown in Fig. 6.

5. Natural Rubber

The electron micrograph of natural rubber benzene solution sampled on a specimen holder without supporting film is shown in Fig. 7. Macro molecules of rubber seemd to associate each other and looked like a vein of leaf.

Table 1. The properties of viscous colloidal solutions.

No.	Viscous colloid		Concentration (%)	Spinnability (cm)			Elasticity (dyne/cm²)	Viscosity		Electron micrograph
	Solute	Solvent		At 25°C	After heating at 95°C	After ultrasonic irradiation		(Poise)	Relative	
1	Mucilage of *Abelmoshus Manihot*	Water	2.3	40~45	0	0	—	—	—	
			0.21[a]	12[a]	0	0	—	—	18.0[a]	1
2	Slime of laminaria	Water	3.8	20~22	—	—	0.89	16.26	—	3
			1.9	18~20	0	8~10	0.37	6.68	—	
3	Sodium polyacrylate	Water	1.0	25~30	15	22	—	—	—	
			0.5	22~23	10	20	8.44	525.0	—	5
			0.1	2~3	—	—	1.77	19.1	22.4	4
			0.05	1	0	0	0.85	13.2	6.9	
4	Cellulose acetate	Acetone	10.0	60	—	—	—	—	—	6
5	Natual rubber	Benzene	2.0	13~15	—	12~13	0.97	6.21	—	7
6	Mercury sulfosalicylate	water	5.0	10~15	0	—	—	—	—	
			2.5	7~9	0	1	40.5	2×10^{4}	—	
			0.5	3~4	0	0	—	—	5.2	8
			0.25	1	0	0	1.61	333.0	2.4	
7	Mercury anthranilate	Water	0.1	3~4[b]	0	0	0.25	209.0	—	11
8	Agar-agar	Water	0.12[c]	0	0	0	14.6[c]	1×10^{10}[c]		13

[a] Reference 4, [b] After 2 weeks, [c] Reference 3.

6. Mercury Sulfosalicylate

Electron microscopic investigations on mercury sulfosalicylate were reported by a few authors.[1),5)] Mercury sulfosalicylate is a gel which has no spinnability at the concentration above ca. 2 %. The gel becomes a viscous sol which has spinnability by stirring. The electron micrograph of the sol is like network in which threads overlap one another as shown in Fig. 8. The spinnability and the viscosity of mercury sulfosalicylate solution decreased markedly by heating or ultrasonic irradiation, but they restored gradually upon standing at room temperature. The electron micrographs of the solution after heating and ultrasonic irradiation are shown in Figs. 9 and 10. They were changed to granules at 90°C and to little broken networks by ultrasonic irradiation. The network structure was reconstructed in the specimen after a certain lapse of time.

7. Mercury Anthranylate

Mercury anthranylate[6)] was a gel at first, but it changed to a viscous sol, which had the spinnability, by stirring or upon standing over a week. The electron micrograph of every specimen was a collection of thread-like substances as shown in Fig. 11.

8. Agar-agar

Above ca. 0.1 % aqueous agar-agar solution becomes a gel and changes to a sol which has no spinnability by shaking. The electron micrograph is like entangled threads or granules as shown in Figs. 12 and 13. The granules increased with decreasing the concentration of the sol. The thickness of the thread was almost constant and similar with the diameter of the granules (ca. 4 mμ).

CONSIDERATION

The electron micrographs of the viscous colloidal solutions were the network or thread-like structure. It seems that the network which is appeared in the case of sodium polyacrylate etc. was formed during a drying process of the specimen for electron microscopy and the original viscous fluids could not have always such a structure in themselves. However, in the thread-like structure which is obtained from agar-agar solution the thickness of the threads was uniform and a thread was like to be connected with granular matter. At least in agar-agar gel the thread structure constructed from the connection of the granular matter seemed to exist at highly hydrated state. Mercury sulfosalicylate and anthranylate are situated between these two kinds of substances described above. The gels of them have no spinnability,

Electron Micrographs of Viscous Colloidal Solutions

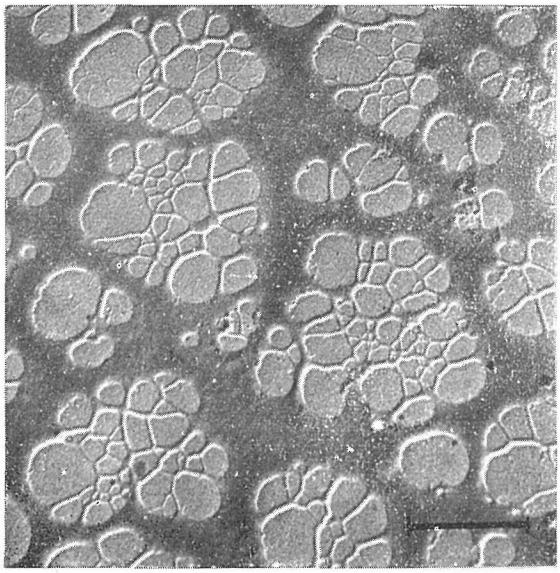

Fig. 1. Mucilage of *Abelmoshus Manihot* (0.21 % aqueous solution). (Cr-shadowing, × 15,000)

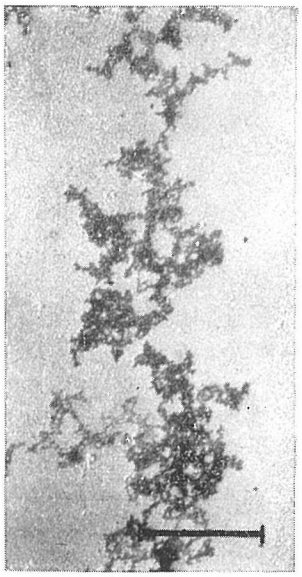

Fig. 2. Mucilage of *Abelmoshus Manihot* (after heating). (Cr-shadowing, × 15,000)

Fig. 3. Slime of laminaria (1.9 % aqueous solution). (Cr-shadowing, × 15,000)

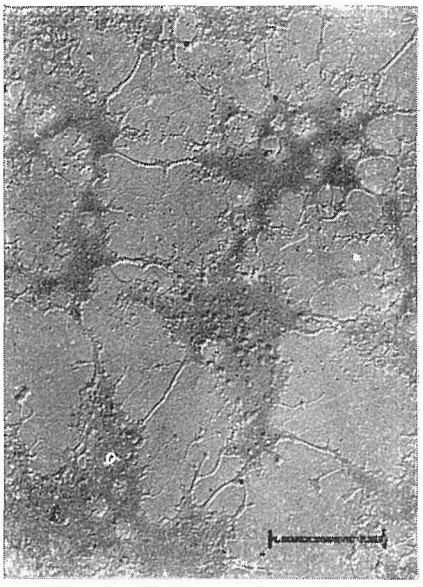

Fig. 4. Sodium polyacrylate (0.1 % aqueous solution). (Cr-shadowing, ×15,000)

Electron Micrographs of Viscous Colloidal Solutions

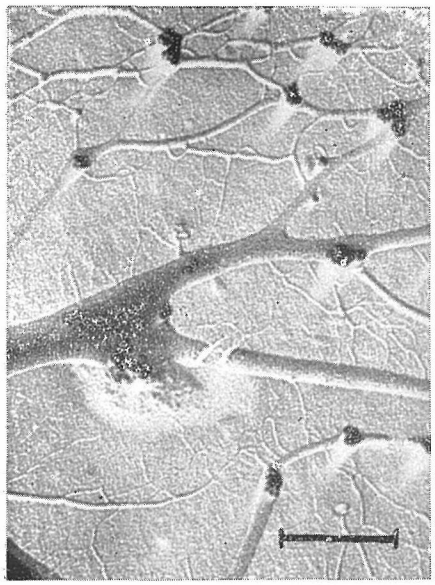

Fig. 5. Sodium polyacrylate (0.5 % aqueous solution). (Cr-shadowing, × 15,000)

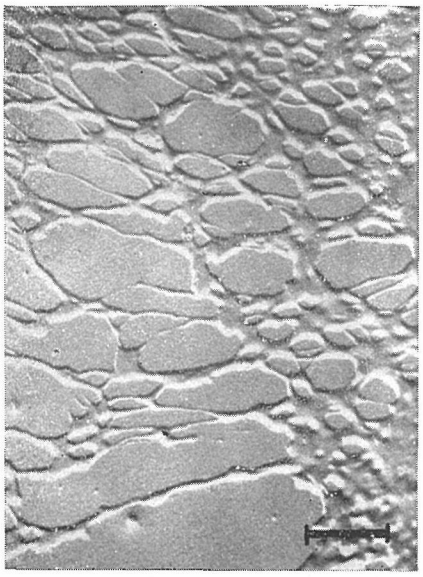

Fig. 6. Cellulose acetate (1 % acetone solution). (Cr-shadowing, × 10,000)

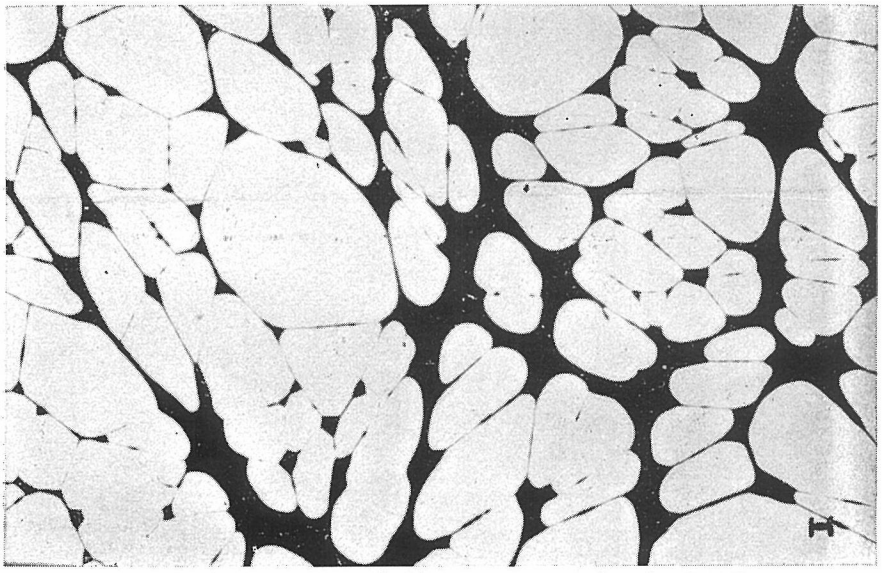

Fig. 7. Natural rubber (2 % benzen solution). (× 3,000)

Electron Micrographs of Viscous Colloidal Solutions

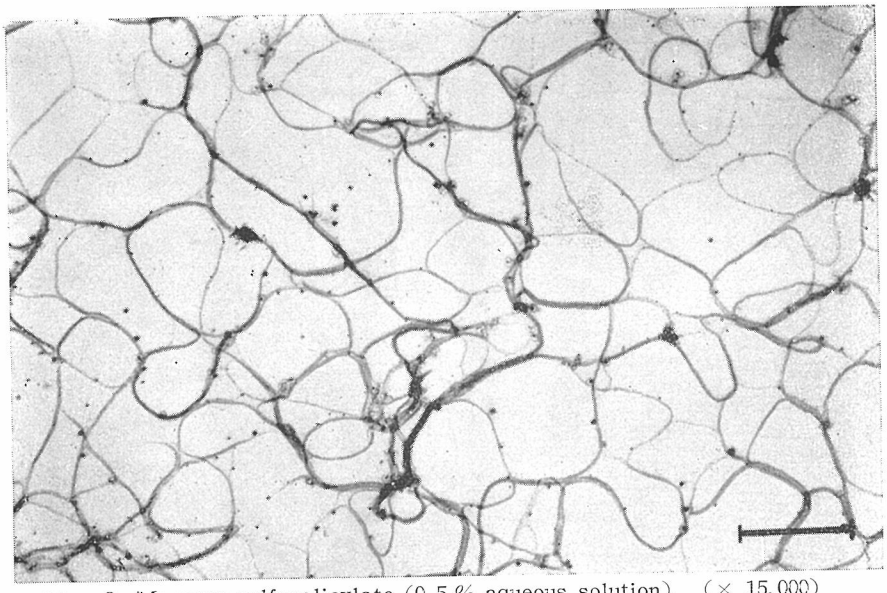

Fig. 8. Mercury sulfosalicylate (0.5 % aqueous solution). (× 15,000)

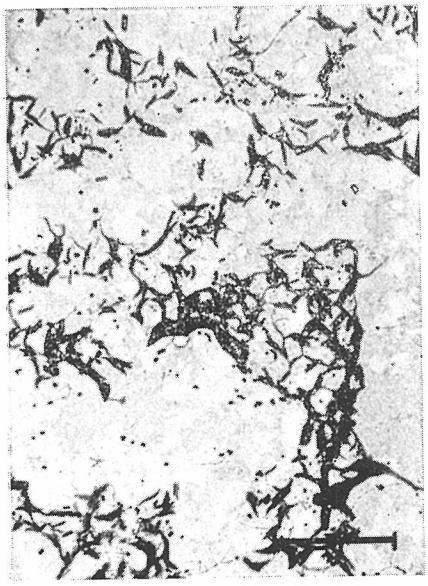

Fig. 9. Mercury sulfosalicylate (0.5 % aqueous solution 95°C). (× 15,000)

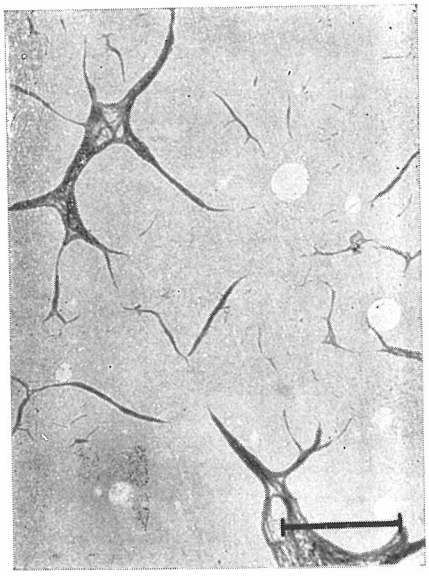

Fig. 10. Mercury sulfosalicylate (0.5 % aqueous solution, ultrasonic irradiation). (×15,000)

Electron Micrographs of Viscous Colloidal Solutions

Fig. 11. Mercury anthranilate (0.1 % aqueous solution). (Cr-shadowing, × 10,000)

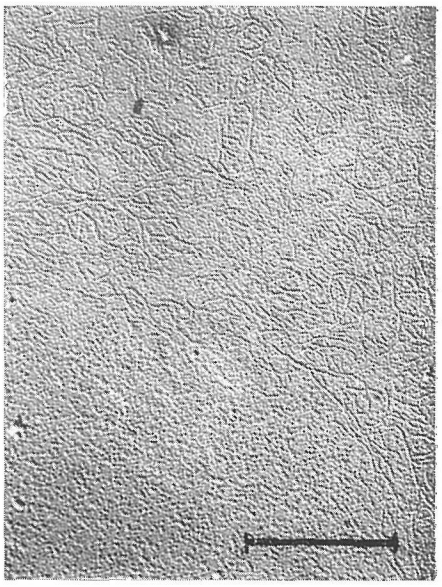

Fig. 12. Agar-agar (0.05 % aqueous solution) (Cr-shadowing, × 20,000)

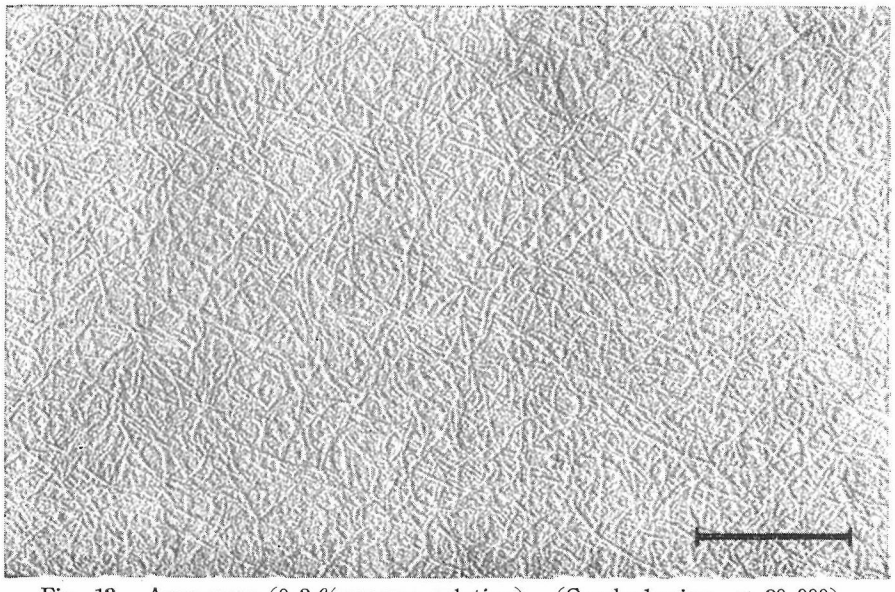

Fig. 13. Agar-agar (0.2 %aqueous solution). (Cr-shadowing, × 20,000)

but it appears in the fluids after stirring. The threads grown from the granules and constructed network structure seemed to exist in the sols or gels of these organo-mercury compounds.

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