Physicochemical Properties of the Surface of Aqueous Solutions. IV. Classification of Mechanical Behavior of Several Aqueous Surfaces*

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In the preceding paper[1] the mechanical behavior of the surface of aqueous solutions was measured and discussed by means of the mechanical models. Further studies on the mechanical behavior of surfaces of aqueous solutions of various substances have been continued from the similar point of view.

Experimental

Measurements of surface rigidity and surface viscosity coefficient were carried out using the same apparatus as described previously.[1] Of the samples used, saponin, crystal violet, polyvinyl alcohol and horse serum albumin were those used in the preceding experiment.[1] Gum arabic, peptone, egg albumin and sodium stearate were commercially pure and were used without further purification. In this experiment, the mechanical behavior of the surface of the solution was studied as a function of concentration. Solutions were prepared using freshly distilled water. The time of aging prior to the measurement was kept to one hour* and the experiments were carried out at room temperature.

Result

The concentration dependence of viscoelastic constants for each system observed was shown in Figures from 2 to 9. In these figures, the ordinates represent G,G' and η which correspond to the elasticity and viscosity constants of a three-parameter model respectively shown in Fig. 1 and the abscissa, the logarithm of concentration, C. The portions of dotted line in $\eta \sim \log C$ curves represent the region of non-Newtonian flow. Here, non-Newtonian flow observed did not always obey the empirical relation,

$$\log\frac{d\theta}{dt} = A - B\theta$$

which was obeyed in the case of the measurement reported in the preceding paper.[1] The temperature range of the experiment was also

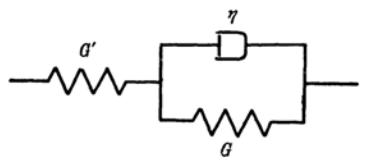

Fig. 1.

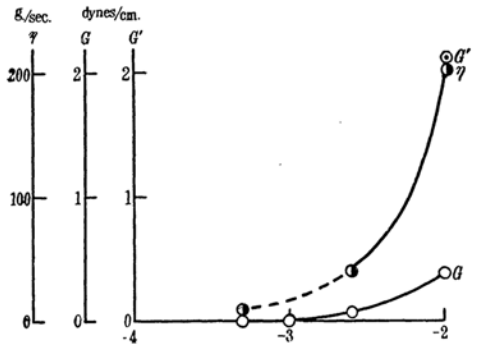

Fig. 2.—Crystal violet solution. 18.5~20.5°C.

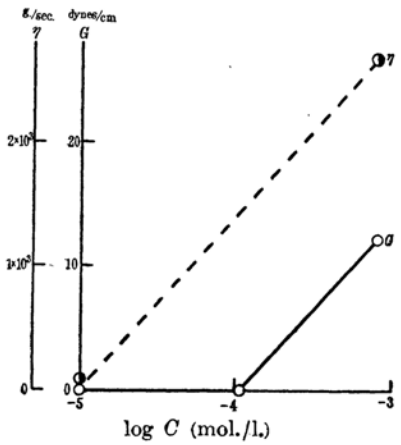

Fig. 3.—Sodium stearate solution. 10.5~11.5°C.

* This work was reported at the meeting for general discussion of colloid chemistry held on Nov. 10, 1951, in Tokyo, under the auspices of the Chemical Society of Japan.

(1) T. Sasaki and H. Kimizuka, This Bulletin, **25**, 318 (1952).

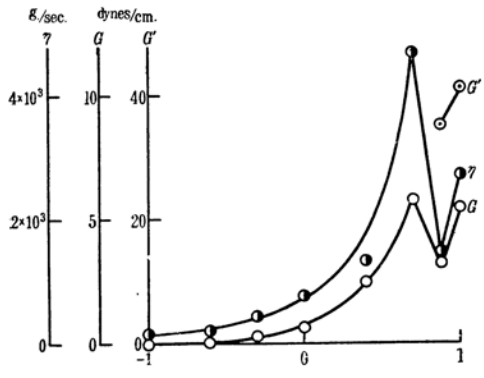

Fig. 4.—Saponin solution. 18.0~20.0°C.

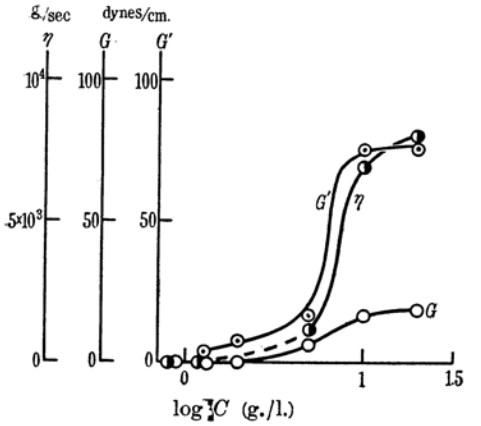

Fig. 5.—Gum arabic solution. 18.0~20.0°C.

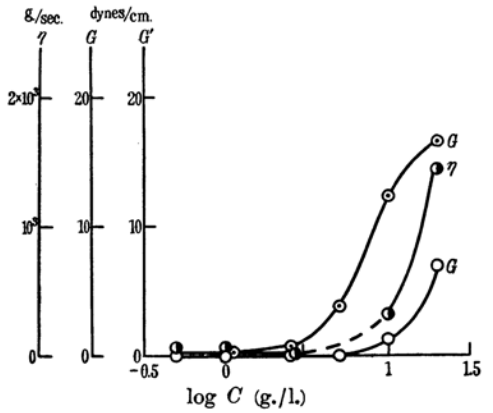

Fig. 6.—Peptone solution. 23.0~25.0°C.

indicated in each figure. The time effect on the mechanical behavior of the surface was also studied, of which an example was shown in Table 1. In Table 2, observed values of the relaxation time, η/G', and the retardation time, η/G, were summarized where T denoted the time scale.

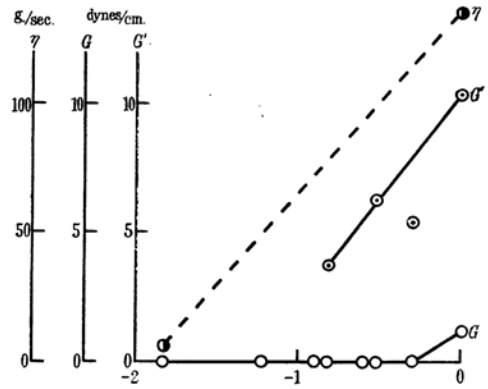

Fig. 7.—Horse serum albumin solution. 23.0~25.0°C.

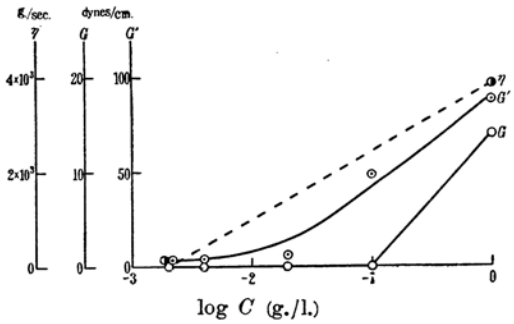

Fig. 8.—Egg albumin solution. 19.5~20.5°C.

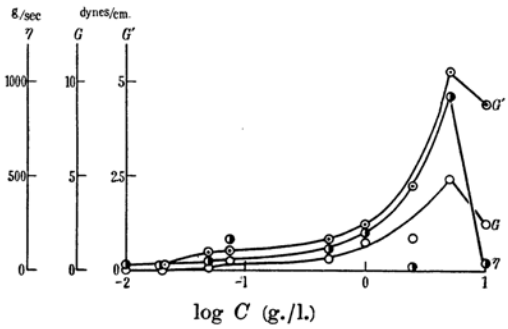

Fig. 9.—Polyvinyl alcohol solution. 18.0~20.0°C

Table 1

Effect of the Time of Aging on the Mechanical Behavior of the Surface of Polyvinyl Alcohol Solution (1.25×10^{-3} g./l.)

Time of Aging of Surface (hrs.)	G' (dyn./cm.)	G (dyn./cm.)	η (g./l.)
1		0.00	~0.00
2		0.00	0.03
3	5.11×10^{-4}	0.00	1.62
10	3.30×10^{-2}	1.23×10^{-2}	0.42

Table 2

Comparison between the Time Scale and Retardation Time or Relaxation Time

Model	η/G' (sec.)	η/G (sec.)
Three-parameter model	5.0—810$\sim T$	3.6—535$\sim T$
Maxwell model with non-Newtonian flow	$\sim$	$>$
Maxwell model	0.8—7.8$\sim$	$\gg$
Voigt model	$\ll$	90—1440$\sim$
Non-Newtonian flow	$\ll$	$>$
Non-Newtonian flow	$<$	$\gg$
Newtonian flow	$\ll$	$\gg$

Discussion

As seen in the results shown in the Figures from 2 to 9, a type of mechanical model for a given solution generally changed with the increase in concentration, presumably due to the change in the mechanical structure of the surface layer. This change ocurred in the following two ways in the present experiment.

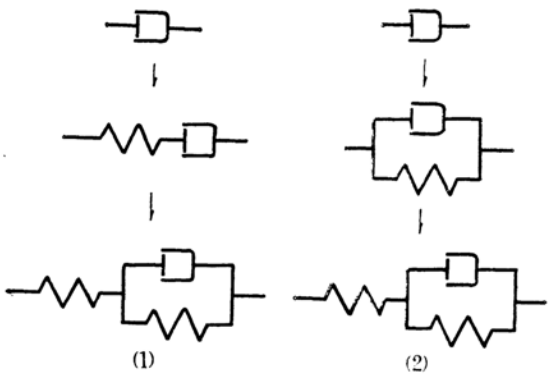

Fig. 10.—Mode of transformation in mechanical behavior of surface.

Surfaces of solutions of high polymers, such as egg albumin, horse serum albumin, peptone, gum arabic and polyvinyl alcohol changed according to the mode 1,* while those of sodium stearate, crystal violet and saponin, the mode 2. Among the substances of the mode 2, sodium stearate did not exhibit the mechanical behavior of three-parameter model under the condition of one hour aging. Prolonged aging, however, made it to be realised, as in the case of fifty hour's aging of 1 g./l. solution where $G'=7.03$ dyn./cm. $G=0.45$ dyn./cm. and $\eta=188$ g./sec. The author should like to take the opinion that this difference in the mode of change in a mechanical model is likely to come not from the difference in molecular structure of corresponding substances, but from that in the structure of higher order, for instance, whether it is a high polymeror a micelle. This requires further confirmation since it is not clear at present.

As seen in Table 1, a change in the time of aging without changing concentration caused such a change in mechanical model as that produced by the change in concentration with constant aging. From this, we can presume that the solute is gradually accumlating at the surface of the solution in the course of time and that the mode of change in a mechanical model with concentration generally does not change with the time of aging.

Table 2 shows the relaxation and retardation times observed which are of course the same order of magnitude to the time scale of the present experiment, in agreement with the requirement of the theory of viscoelasticity.(2) This table also shows the correspondence between the mode of change with concentration in the mechanical model and the process in which relaxation time and retardation time, starting from a much smaller or larger value for the viscous flow, approach the order of the magnitude of the time scale of the experiment.

Summary

1. Mechanical behaviors of surfaces of aqueous solutions were studied, and were explained by the three-parameter model with various relaxation times and retardation times.

2. The mode of change of mechanical models with the increase in concentration of the solution were classified into two groups; a change from the dashpot through the Voigt model to the three-parameter model, and a change from the dashpot through the Maxwell model to the three-parameter model. Saponin, crystal violet and sodium stearate belonged to the former, and egg albumin, horse serum albumin, peptone, gum arabic and polyvinyl alcohol, to the latter. It was presumed that this difference was due to the difference in the state of aggregation of their molecule.

* Inokuchi, however, reported somewhat different results on the monolayer of egg albumin and horse serum albumin, in which the Maxwell model was not observed (The annual meeting of the Chemical Society of Japan, Tokyo, on April, 1952.).

(2) T. Alfrey Jr., "Mechanical Behavior of High Polymers", Interscience Publisher, Inc., New York, 1948, p. 116.

In conclusion, the author wishes to express his sincere thanks to Prof. T. Sasaki for his guidance and encouragement given to the author during this experiment. A part of the cost of this research has been defrayed from the Scientific Research Expenditure of the Ministry of Education given to the professor.

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