The Influence of Heat Treatment on the Solidification Time of the Reversible Sol-Gel Transformation of Gelatin

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In a previous paper it was mentioned that the solidification time of the reversible sol-gel transformation of the sols of silicic acid, of agar-agar and of gelatin is noticeably shortened by heat treatment.[1] The characteristic feature of this phenomenon can be expressed by the formula:

$$T_1 > T_2 \qquad (1)$$

where T_1 = the thixotropic solidificaticn time, and

T_2 = the solidification time under heat treatment.*

The term "thermopexy," on the model of rheopexy, has been suggested for this phenomenon, indicating that the gelation tendency of thixotropic sol is accelerated by heat treatment.

Lately, however, we have realized that neither the qualification nor the method of preparing the gelatin in the previous experiment was adequate and that the conclusion obtained needed to be corrected. From a comparison of the results of the reinvestigation of gelatin with the data on silicic acid and agar-agar, we came to the following conclusion on the influence of heat treatment: there are two modes in thermopexy, positive and negative, the former being the case with silicic acid and agar-agar, and the latter with gelatin.

Experimental and Discussion

The characteristics of the gelatin used in the experiment are as follows: Water content, 17% wt.; isoionic point, 4.85; viscosity, 5.7 centipoise (measured for 4.2% sol at 35°C by using an Ostwald viscosimeter); rigidity, 4.1×10^5 dyn./cm^2 (measured for the 4.2% gel obtained by keeping the sol 8 hr. at 0~1°C).

The experiments are carried out as follows. Six grams of the gelatin is put into a beaker with 400 ml. of water and is left to stand 2 hr. at room temperature. Swelling takes place. The beaker is then kept at 50°C for 30 min. The swollen gelatin turns out to be a homogeneous sol. The total weight of the sol is then made 500 g. by adding water. Thus we get the gelatin sol of the concentration 1%, i.e., 1 g. gelatin per 100 g. of the sol. Ten milliliters of the sol is put into each of the 20 test tubes, each with a radius 13.5~14 mm. The test tubes are then left to stand at room temperature (10~15°C). The sol changes into a gel which does not flow out, even when the test tube is placed upside down. All of the test tubes are shaken by hand, and the gel in them is brought into sol. The test tubes are then divided into two groups. (a) 10 test tubes are left to stand at room temperature and are used for the study of the thixotropic solidification time, T_1. (b) The other 10 test tubes are used for the study of T_2. They are put into a water bath of 50°C for 2 min. and then left to stand at room temperature; the resulting change is observed. The temperature of 50°C was chosen in order to avoid the denaturation of gelatin. The test tubes (a) and (b) are tilted one after another at certain time intervals, and the resulting decrease in fluidity is observed. The time at which the sol ceases to flow is taken as the solidification time. The average values of T_1 and also of T_2 are taken.

The influence of foreign substances was also studied. Urea and KSCN were chosen as the substances which destroy the hydrogen bond, and $KAl(SO_4)_2$ as the substance which forms bridges between gelatin molecules. The results are summarized in the following table.

Foreign substance	Concn. of the foreign substance mol./1000 g. sol	T_1 min.	T_2 min.	Concn. of sol g./100 g. sol
None	—	25	140	1
$CO(NH_2)_2$	0.1	30	170	1
	0.5	50	225	1
KSCN	0.1	25	140	1
$KAl(SO_4)_2$	0	95	220	0.8
	0.005	80	190	0.8
	0.01	50	180	0.8
	0.02	35	150	0.8

We see that in all cases

$$T_1 < T_2 \qquad (2)$$

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[1] T. Katsurai and K. Inouye, *Kolloid-Z.*, **142**, 162 (1955).

* For the sake of convenience T_1 is taken as the standard in this article; the change of T_2 is discussed relative to T_1.

This is just the opposite of (1). This means that the influence of heat treatment on the solidification time in the case of gelatin appears in the reverse (or negative) direction as compared with the case of silicic acid and that of agar-agar. Repeated experiments with the same sample gave the same result. Although both T_1 and T_2 increase with the rise in room temperature, relation 2 is still satisfied.

The presence of urea in the sol increases T_1 and T_2. If the concentration of urea exceeds 1 M per 1000 g., the sol does not set into a gel and it becomes impossible to carry out the experiment. In the case of KSCN, the experiment becomes difficult when the concentration exceeds 0.5 M per 1000 g. because of the enormous increase in solidification time. The presence of $KAl(SO_4)_2$ in the sol greatly decreases T_1 and T_2. Thus the experiment was carried out with a sol of a smaller concentration and a small amount of the salt.

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