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Abstract

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ON THE MECHANISM OF GELATION IN GELATIN SOLUTIONS

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Although a large number of works have been devoted to the study of gelation [1–6], a number of problems connected with the mechanism of this process still remain unexplained. The aim of the present work was to study the processes of structure formation in gelatin solutions.

We based our work on the studies of P. A. Rehbinder and his school [7–10] on elucidating the mechanism of the processes of development of spatial structures of various types in suspensions, colloidal solutions, and polymer solutions.

To investigate the mechanism of gelation it is necessary to study the kinetics of growth of the strength of the spatial structure with time [7,16] and its capacity for reversible recovery after destruction. In addition, by studying optical rotation in gelatin solutions, one can determine the conformational state of its molecules [14,15].

The kinetics of structure formation was investigated from the increase in strength—the limiting static shear stress (P_k) of the structure developing in the gel. For this purpose the method of the tangentially displaced plate according to Weiler–Rehbinder was used [12].

To eliminate slipping, plexiglass plates with a corrugated surface (with sharp horizontal notches), 2 cm high and 1.5 cm wide, with a depth of 1 mm, were used. The plates were placed in the middle of rectangular cuvettes of square cross section with a side of 3 cm and a height of 5 cm.

The cuvettes were filled with a hot gelatin solution, and immediately, with the aid of a special device, the plate was lowered into the middle of the cuvette. The cuvettes with the plate were placed in a desiccator with water and stored in a refrigerator at a temperature of +5°. Subsequently, a series of such cuvettes filled with gelatin solutions of different concentrations was kept for the required time under various conditions in a thermostat. The plate, with the aid of a reduction stage, was displaced vertically at a low constant speed. The limiting forces were measured with a set of elastic rods,

$$P_k = F_k/2S,$$

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

where S is the area of the plate.

The experiments were carried out on "Photo" grade gelatin, which was purified and brought to the isoelectric state by Loeb' s method. The gelatin solutions were prepared by the usual procedure [11].

From Fig. 1 it is evident that the gelation process proceeds in two stages: 1 —the induction period, during which the strength of the system remains very small, not exceeding hundredths of a dyne/cm^2, and 2—the stage at which the strength of the system gradually increased, reaching its maximum value (about 1.2 dyne/cm^2) by 4 days. The induction period of structure formation was 30 min at 6°, 3 h at 12°, and 6 h at 19°. According to the data of Doty and Boedtker [13], at this stage aggregates are formed from gelatin molecules. By the time the greatest strength is reached, i.e., by the completion of gelation, the process of mutarotation also ends—the greatest (with time) specific optical rotation is attained (see Fig. 2), i.e., the greatest degree of helicity of the gelatin molecules.

To determine the influence of the helical conformation on the strength of the structure of a gelatin gel, urea, which destroys the helical conformations of gelatin molecules, was added to the solutions. Measurements of the specific optical rotation showed that the gelatin molecules are in the conformation of a statistical coil. In the presence of urea additives, a gel is not formed in gelatin solutions ([6,17]). From this experiment one could conclude that the helical conformation of gelatin molecules determines the strength of the structure. But the strength of the gel structure is determined not only by conformation, but also by the number of bonds unambiguously determined by the conformation of the macromolecules and by the strength of these bonds. As was shown earlier ([15]), the structure of gels with concentrations from 1 to 20% is formed mainly by hydrogen bonds, which arise in the process of gelation. Since both the helical conformations of the gelatin molecules themselves and the three-dimensional network of the gel are held together by hydrogen bonds, there evidently exist optimum conditions for obtaining a gel of the greatest strength.

Fig. 1. Increase in the limiting shear stress of a 1% gelatin gel in the isoelectric state (pH 5) at various temperatures: 1 —6°, 2 —12°, 3 —19°

Fig. 2. 1 —increase in the limiting shear stress of a 1% gelatin gel in the isoelectric state at 6°; 2 —change in the specific rotation of the same gel

Fig. 3. Increase in the strength of a 1% gelatin gel, destroyed at different stages of its formation in the isoelectric state at 6°: 1 —undestroyed structure,

Fig. 3

Figure 3: Fig. 3

2 —destroyed after 4 hours, 3 —after 1 day, 4 —after 5 days

According to the classification of P. A. Rehbinder ([8]), spatially structured systems may be divided into two types: coagulation systems (thixotropically reversible), with weak structural bonds, and condensation-crystallization systems (irreversibly destroyed), with strong bonds.

To determine the type of structure arising in gelatin gels, we investigated the increase in strength in a structure destroyed at different stages of its formation ([7,16]). The results are presented in Fig. 3. Curve 1 shows the increase in strength of a 1% gelatin gel, while curve 2 characterizes the process of gelation in a gelatin solution destroyed after 4 hours. In such a destroyed gel there is a process of increasing strength, but the resulting strength is less than that of the undestroyed gel. Curves 3 and 4 characterize the increase in strength of structures destroyed after 1 and 4 days. In such systems, under repeated destruc-

[[unclear: beginning of paragraph]] completely reversibly, structures with the same low strength (0.2 g/cm^2) again develop. Consequently, in such systems a weak coagulation structure arises, similar to ordinary thixotropic structural networks, in which aggregates of macromolecules are bound by van der Waals forces, apparently between hydrophobic (hydrocarbon) groups of gelatin molecules ([2]). The coagulation character of the structure at this stage is confirmed by its complete reversibility upon mechanical destruction.

In contrast to coagulation structures, the considerably stronger condensation-crystallization structures are destroyed irreversibly under mechanical action. Thus, the structures formed in a gelatin gel should be regarded as condensation-coagulation structures. The increase in the strength of the gelatin structure with time and the different degree of recovery of the strength of the gelatin structure upon destructions at different stages of its formation indicate that bonds of different character participate in the formation of gelatin gels. Irreversibly destroyed hydrogen bonds arise only in the process of formation of helical conformations of gelatin molecules; these bonds mainly determine the strength of a 1% gelatin gel. Van der Waals forces between hydrophobic, hydrocarbon groups of the molecules also make their contribution to the structural-mechanical properties of the gelatin gel; in magnitude this contribution to the strength of the structure is an order of magnitude smaller, but it provides the thixotropy of the gel.

The partial recovery of the strength of a gel destroyed after a short interval of time from the beginning of structure formation (Fig. 3, curve 2) is not thixotropic in character, but is connected with the fact that conditions exist for the formation of hydrogen bonds, both intramolecular and intermolecular.

This phenomenon is analogous to that observed, for example, during structure formation in an aqueous suspension of hemihydrate gypsum, where recovery of the structure after destruction was ensured by the presence of supersaturation and by the possibility, under such conditions, of forming intergrowth contacts between crystals of the hydrate newly formed ([16], [18]).

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Note: Figure translations are in progress. See original paper for figures.