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Radiation Chemical Studies of Protein Reactions: Effect of Alkaline-Earth Metals on the Breaking of Secondary Bonding in Protein

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ABSTRACT

The radiation protective effect of the breaking of secondary bonding in protein was examined with alkaline-earth metals such as magnesium chloride, calcium chloride, strontium nitrate, and barium chloride, and alkaline metals and heavy metals such as lithium chloride, sodium chloride, potasium nitrate, ferrous chloride, ferric sulfate, nickel sulfate, aluminum nitrate, and zinc sulfate. An empirical equation for the viscosity change was obtained.

INTRODUCTION

It is well known that some alkaline-earth metals such as calcium interact with some biological macromolecules such as protein [1], and that they also protect the change of permeability of some biological membranes such as cell membranes induced by radiation [2, 3].

The effect of alkaline-earth metals such as magnesium chloride, calcium chloride, strontium nitrate and barium chloride against radiation on biological macromolecules such as protein is of interest since structural changes in the biological macromolecules were caused by the breaking of inter- or intramolecular bonds [4]. It was therefore decided to investigate the effect of the alkaline-earth metals against radiation on the breaking of secondary bonding in protein.

The breaking of hydrogen bonds in gelatin molecules caused by urea was selected as the breaking of secondary bonding in protein [5-7]. The determination can be followed by measuring the viscosity of the solution as a function of the alkaline-earth metal concentration.

EXPERIMENTAL

Materials

The gelatin and urea used in this work were the same as those described in a previous paper [6].

The magnesium chloride, lithium chloride, ferrous chloride, ferric sulfate, and aluminum nitrate used were commercial materials produced by Kanto Chemical Co., Inc.

The calcium chloride, strontium nitrate, and zinc sulfate used were commercial materials produced by Junsei Pure Chemical & Co., Ltd.

The barium chloride and potassium nitrate used were commercial materials produced by Wako Pure Chemical Industries, Ltd.

The sodium chloride used was a commercial material produced by Koso Chemical Co., Ltd.

Apparatus and Procedure

An irradiation source containing about 1500 Ci of ^{60}Co was used. The dose rate in this work was 1.2 × 10^4 R/hr. Solid gelatin was irradiated in air at room temperature. The irradiated solid gelatin was dissolved with urea solution containing the salt of an alkaline-earth metal or a control metal. The viscosity was then measured [7].

RESULTS

The effect of salt of an alkaline-earth metal and of a control metal on the breaking of secondary bonding in protein irradiated by γ-rays (10^3 R) was studied with a 5% gelatin in 8 $\underline{M}$ urea at 30°C.

The alkaline-earth metal used, i.e., magnesium chloride, calcium chloride, strontium nitrate, or barium chloride, and the control metal used, i.e., alkali metals and heavy metals such as lithium chloride, sodium chloride, potasium nitrate, ferrous chloride, ferric sulfate, nickel sulfate, aluminum nitrate, or zinc sulfate, were selected because their compounds are well known.

In the presence of the salt of an alkaline-earth metal the reduced viscosity of gelatin solutions decreased in a linear fashion when a logarithmic abscissa for the alkaline-earth metal concentration in percent, as shown in Fig. 1, was adapted.

In the presence of the salt of a control metal, the reduced viscosity

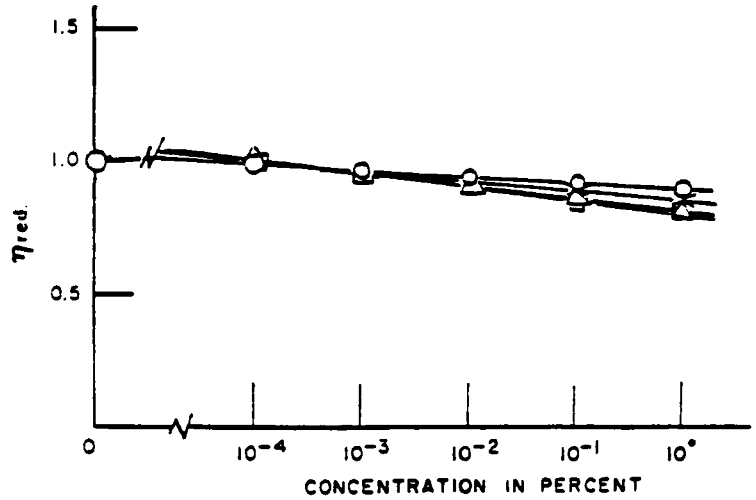

FIG. 1. Dependence of the protective effect on the concentration of salt of alkaline earth metal: (○) magnesium chloride, (△) calcium chloride, (×) strontium nitrate, and (=) barium chloride; 5% gelatin in 8 M urea, 10^5 R, and 30°C.

of gelatin solutions did not decrease, as shown in Figs. 2 and 3.

From these results it is clear that the effect of the alkaline-earth metal on the viscosity is apparently related to its protection of the breaking of secondary bonding in protein.

DISCUSSION

The viscosity change required for the breaking of hydrogen bonds was estimated from Figs. 1-3. Thus the relation between the viscosity change and the concentration of the salt of an alkaline-earth metal is related to that between the breaking of hydrogen bonds and its inhibition. When the concentrations of gelatin and urea and the radiation dose are all constant, the increase in the concentration of the salt of an alkaline-earth metal results in a decrease in the activation required for the breaking of hydrogen bonds in gelatin molecule; see Fig. 1. This behavior indicates that the salt of an alkaline-earth metal protects the gelatin molecule from structural change as a result of scission of hydrogen bonds activated by γ-radiation [6]. Since the increase of the concentration of the salt of an alkaline-earth metal in percent decreases the values of the reduced viscosity of a gelatin molecule, the protection

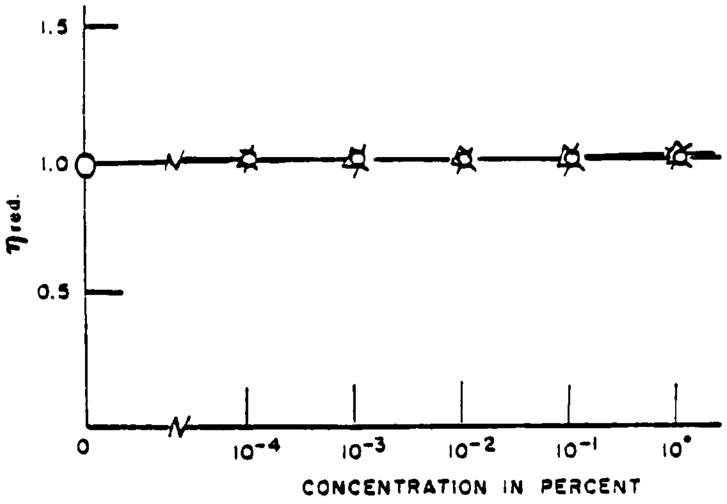

FIG. 2. Dependence of the protective effect on the concentration of salt of alkali metal: (○) lithium chloride, (△) sodium chloride, and (×) potasium nitrate; 5% gelatin in 8 M urea, 10^3 R, and 30°C.

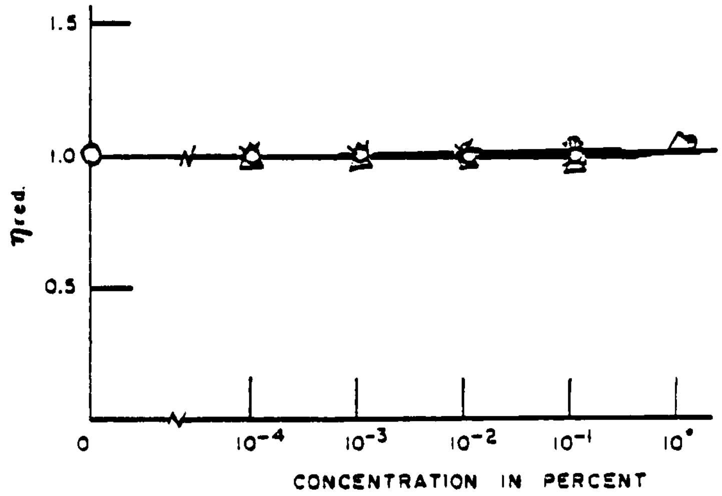

FIG. 3. Dependence of the protective effect on the concentration of salt of heavy metal: (○) ferrous chloride, (△) ferric sulfate, (×) nickel sulfate, (□) aluminum nitrate, and (●) zinc sulfate; 5% gelatin in 8 M urea, 10^3 R, and 30°C.

against scission of hydrogen bonds activated by γ-radiation must be due to the presence of the alkaline-earth metal. At the concentrations studied, protection against scission of hydrogen bonds by the alkaline-earth metal may be due to the interaction of the alkaline-earth metal ion with the activated gelatin molecules formed by irradiation before they can attack the urea, or by interaction with either gelatin molecule. The following process was assumed for the protective reaction:

$$\mathrm{P{-}P} \xrightarrow{h\nu} \mathrm{P^*} + \mathrm{P^*}$$

$$\mathrm{P^*} + \mathrm{S} \longrightarrow \mathrm{P{-}S{-}P}$$

where P—P is the gelatin molecule, P* is the activated gelatin molecule, ,S is the alkaline-earth metal ion, and P—S—P is the linkage between the alkaline-earth metal ion and the gelatin molecule. The role played by the alkaline-earth metal in the process may be understood if one assumes that it decreases the repulsion between the electrical changes on the gelatin molecules and permits them to approach more closely. If hydrogen bonds between the activated groups on the irradiated gelatin molecules were important in causing the breaks, one would expect that the alkaline-earth metal ions would inhibit the breaking, since they should moderate the activated groups either by direct combination with them or by surrounding them with an atmosphere of ions.

The observed reduced viscosity for the system is expressed in linear fashion by adapting a logarithmic abscissa for the concentration of the salt of the alkaline-earth metal in percent:

$$\eta_{\mathrm{red}} = b - a \log X$$

This formula agrees with the experimental data that describe the lines in Fig. 1. This behavior of the salt of an alkaline-earth metal shows a similar dependence on the concentration as was shown in earlier experiments [7].

In this mechanism the alkaline-earth metal ion may be bound at the peptide O and N of the gelatin molecule, and it protects against scission of hydrogen bonds in the gelatin molecule by radiation.

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