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Radiation Chemical Studies of Protein Reactions: Effect of Alkaline-Earth Metals on Optical Rotation

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ABSTRACT

Magnesium chloride, calcium chloride, strontium nitrate, and barium chloride were found to protect against changes in the internal relationships of the atoms in the protein molecule from radiation damage. The optical rotation behavior closely resembles that of amino acids by showing a similar dependence on the concentration.

INTRODUCTION

It is well known that some alkaline-earth metals such as calcium, interact with some biological macromolecules, such as proteins [1], and that they also protect some biological macromolecular membranes, such as cell membrane, against changes of permeability induced by radiation [2, 3]. Since magnesium chloride, calcium chloride, strontium nitrate, and barium chloride are well-known alkaline-earth metals, it was thought desirable to see 1) whether they showed such a protective property and 2) what the effect of their concentration on changes in the internal relationships of the atoms in protein molecule would be.

The urea denaturation of protein was selected as the change in the internal relationships of the atoms in the protein molecule because it has been described in previous papers [4, 5]. The determination can be followed conveniently by measuring the optical rotation of the solution as a function of the concentration of the alkaline-earth metal.

EXPERIMENTAL

Materials

The albumin and urea used in this work were the same as those described in a previous paper [4].

The magnesium chloride, lithium chloride, ferrous chloride, ferric nitrate, nickel sulfate, and aluminum nitrate used were commercial products from the Kanto Chemical Co.

The calcium chloride, strontium nitrate, and zinc sulfate used were commercial products from the Junsei Pure Chemical & Co.

The barium chloride and potassium nitrate used were commercial products from Wako Pure Chemical Industries.

The sodium chloride used was a commercial product from the Koso Chemical Co.

Apparatus and Procedure

An irradiation source containing about 1500 Ci of ^{60}Co was used. The dose rate was 1.2×10^4 R/hr. The solid albumin was irradiated in air at room temperature. The irradiated solid albumin was dissolved with distilled water and mixed with the urea solution containing the salt of alkaline-earth metal or control metal. The optical rotation was then measured [5].

RESULTS

The changes, with time, in the optical rotation of albumin and a salt of an alkaline-earth metal (magnesium chloride, calcium chloride, strontium nitrate, or barium chloride) or of a control metal (an alkali metal such as lithium chloride, sodium chloride, or potassium nitrate; and a heavy metal such as ferrous chloride, ferric nitrate, nickel sulfate, aluminum nitrate, or zinc sulfate) were studied with 2% albumin in 7 M urea, 10^3 R, and 30°C . The alkaline-earth metal and the control metal used were selected because their metals are well known.

The results are shown in Figs. 1-12. The relationships between

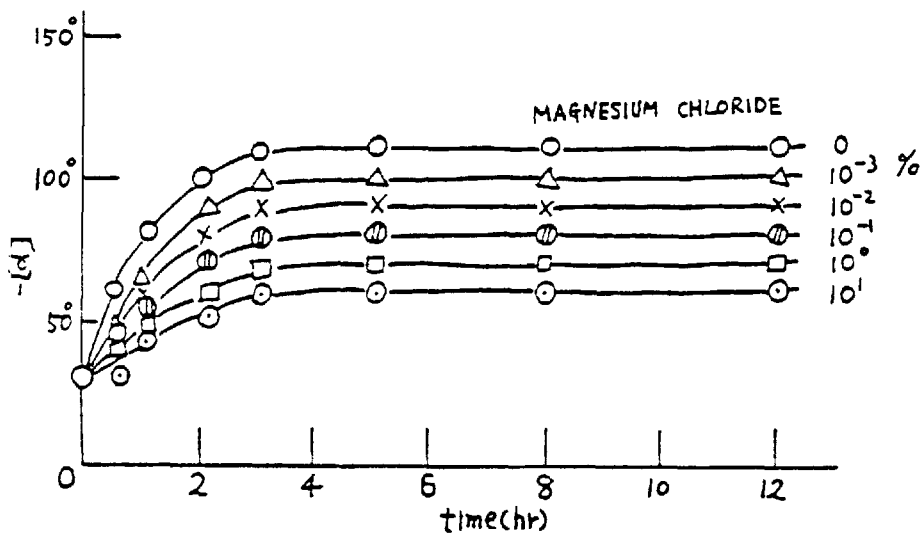


FIG. 1. Specific rotation vs time of 2% albumin in 7 M urea, 10^3 R, and 30° C in the presence and in the absence of magnesium chloride.

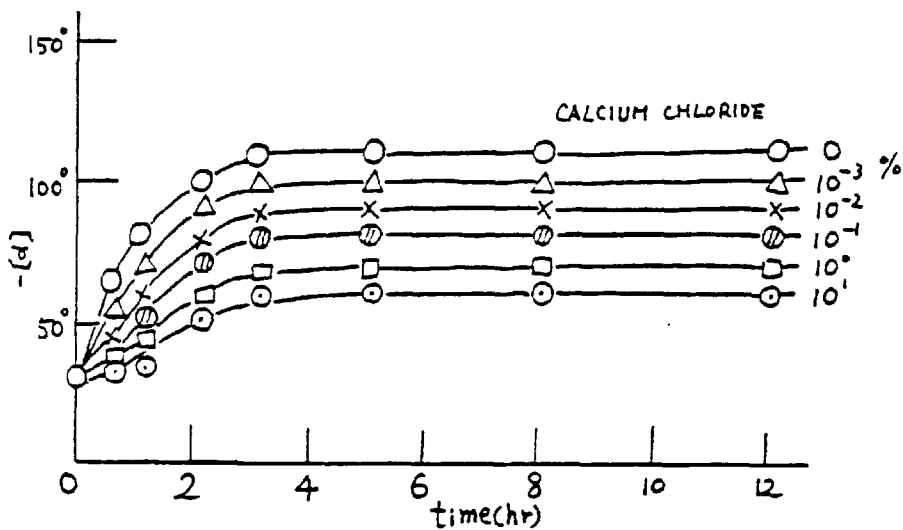


FIG. 2. Specific rotation vs time of 2% albumin in 7 M urea, 10^3 R, and 30° C in the presence and in the absence of calcium chloride.

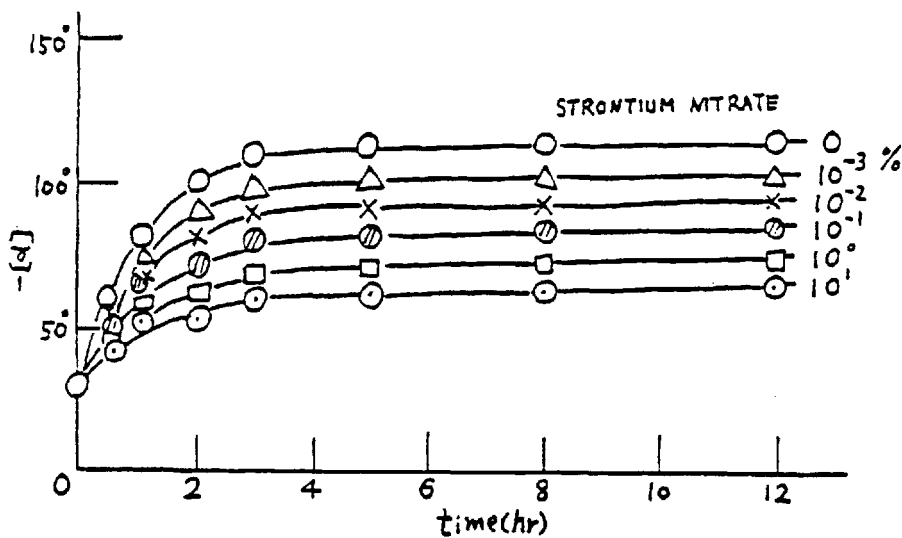


FIG. 3. Specific rotation vs time of 2% albumin in 7 M urea, 10^3 R, and 30° C in the presence and in the absence of strontium nitrate.

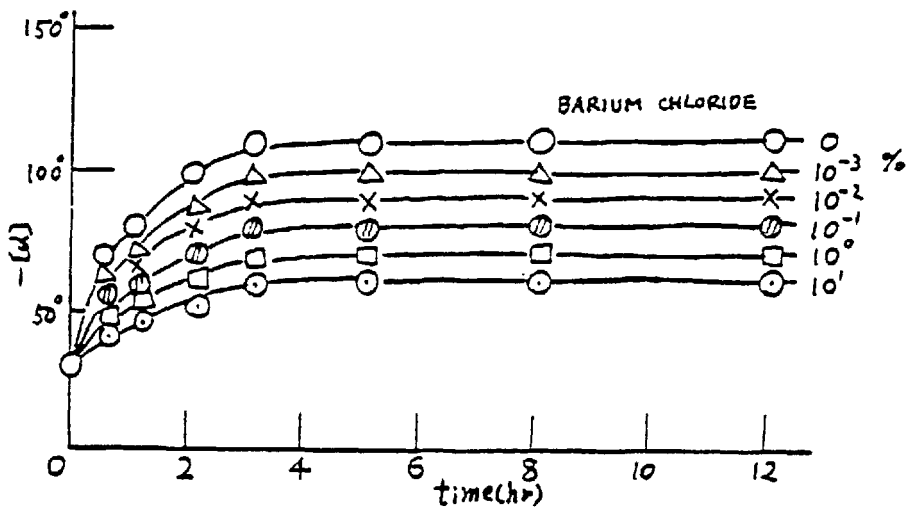


FIG. 4. Specific rotation vs time of 2% albumin in 7 M urea, 10^3 R, and 30° C in the presence and in the absence of barium chloride.

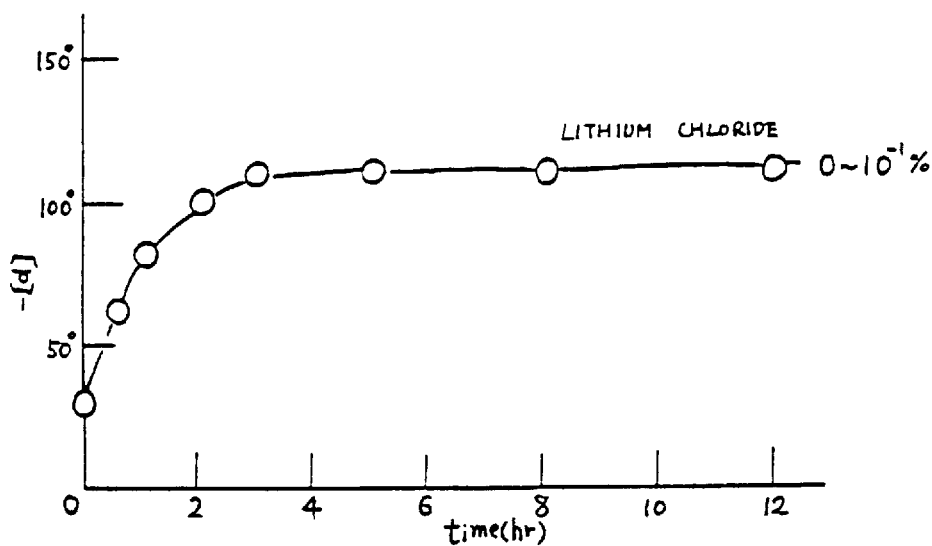


FIG. 5. Specific rotation vs time of 2% albumin in 7 M urea, 10^3 R, and 30° C in the presence and in the absence of lithium chloride.

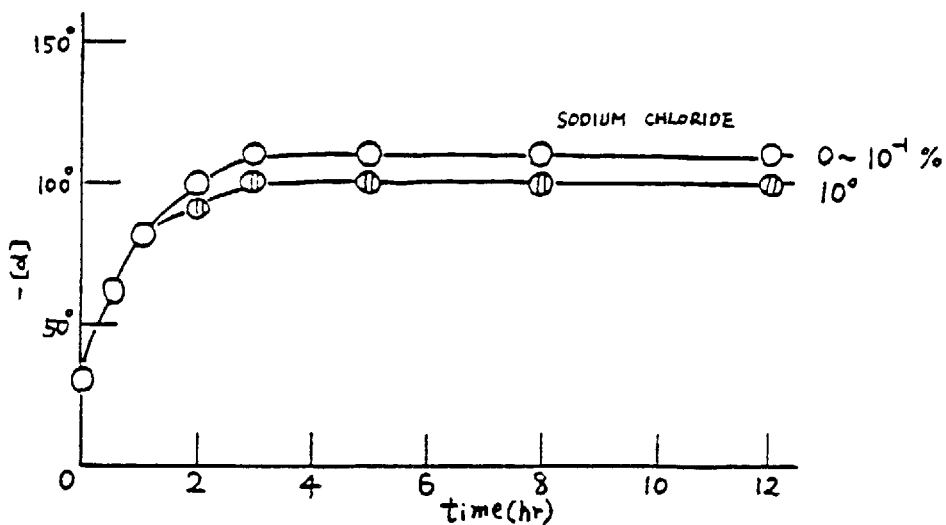


FIG. 6. Specific rotation vs time of 2% albumin in 7 M urea, 10^3 R, and 30° C in the presence and in the absence of sodium chloride.

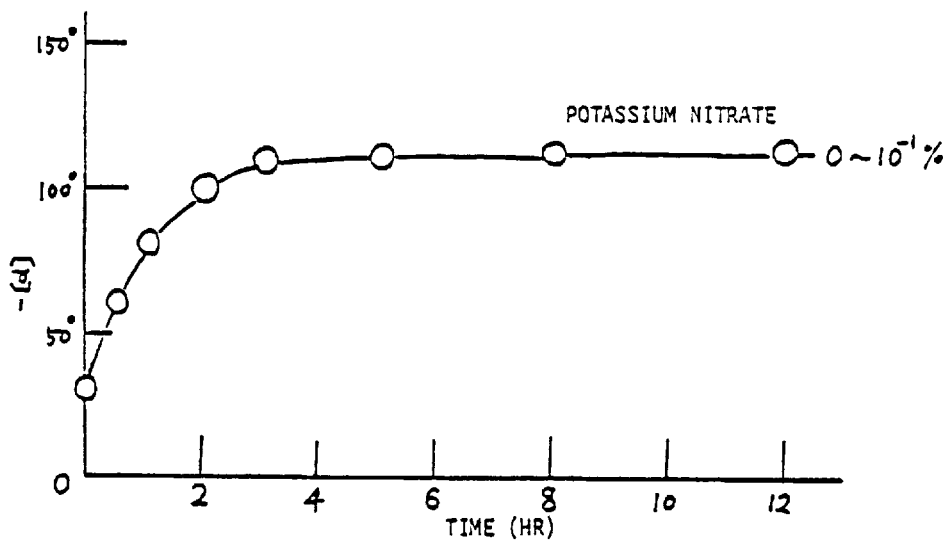


FIG. 7. Specific rotation vs time of 2% albumin in 7 M urea, 10³ R, and 30° C in the presence and in the absence of potassium nitrate.

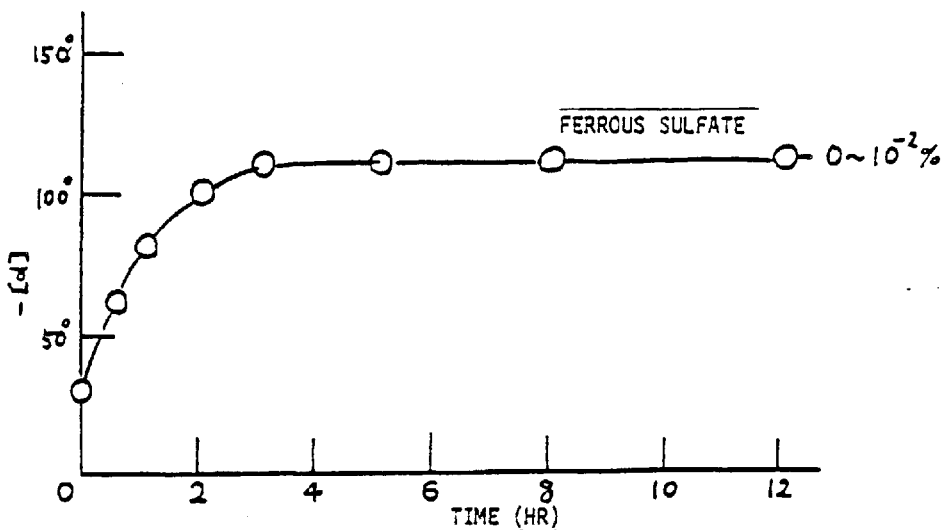


FIG. 8. Specific rotation vs time of 2% albumin in 7 M urea, 10³ R, and 30° C in the presence and in the absence of ferrous sulfate.

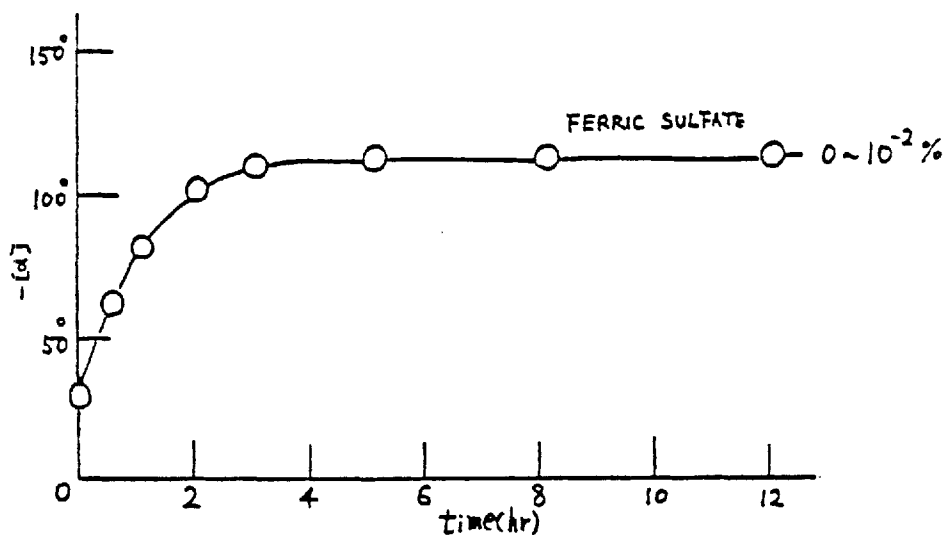


FIG. 9. Specific rotation vs time of 2% albumin in 7 M urea, 10^3 R, and 30° C in the presence and in the absence of ferric sulfate.

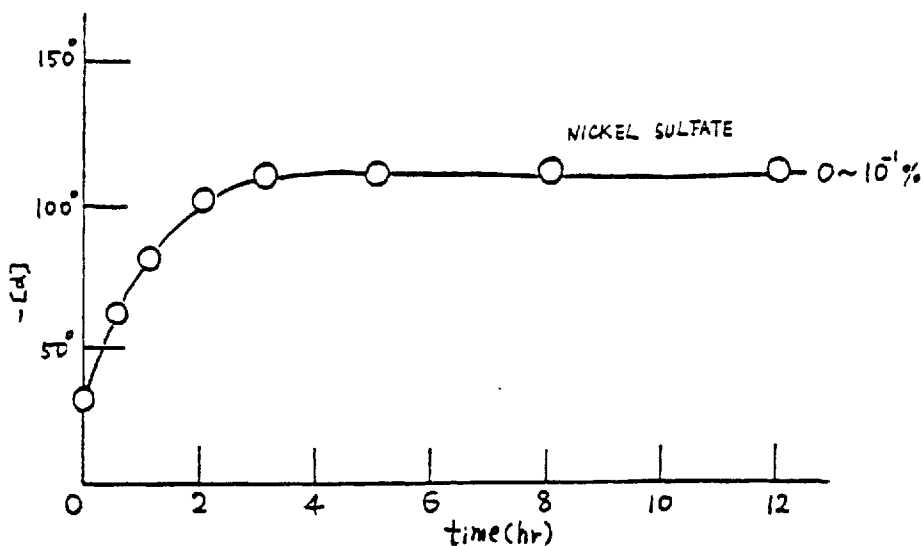


FIG. 10. Specific rotation vs time of 2% albumin in 7 M urea, 10^3 R, and 30° C in the presence and in the absence of nickel sulfate.

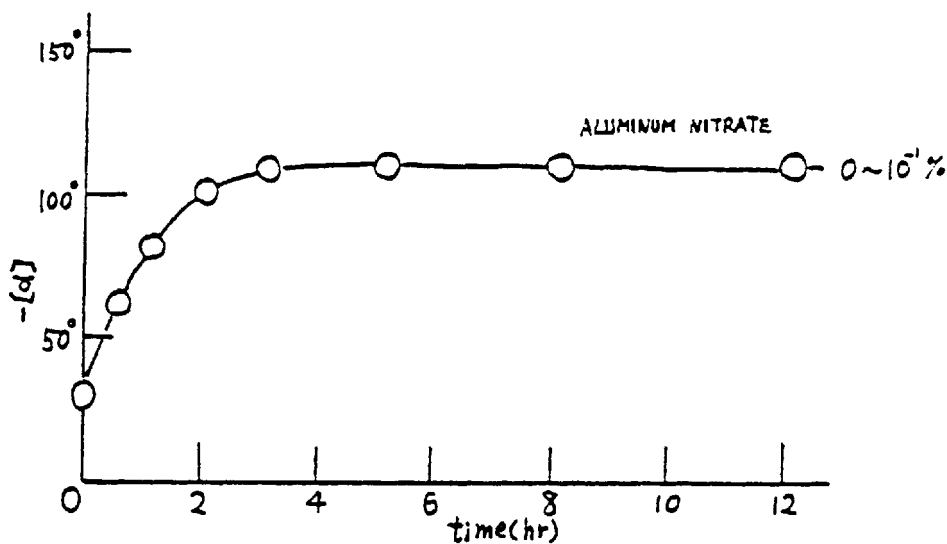


FIG. 11. Specific rotation vs time of 2% albumin in 7 M urea, 10^3 R, and 30° C in the presence and in the absence of aluminum nitrate.

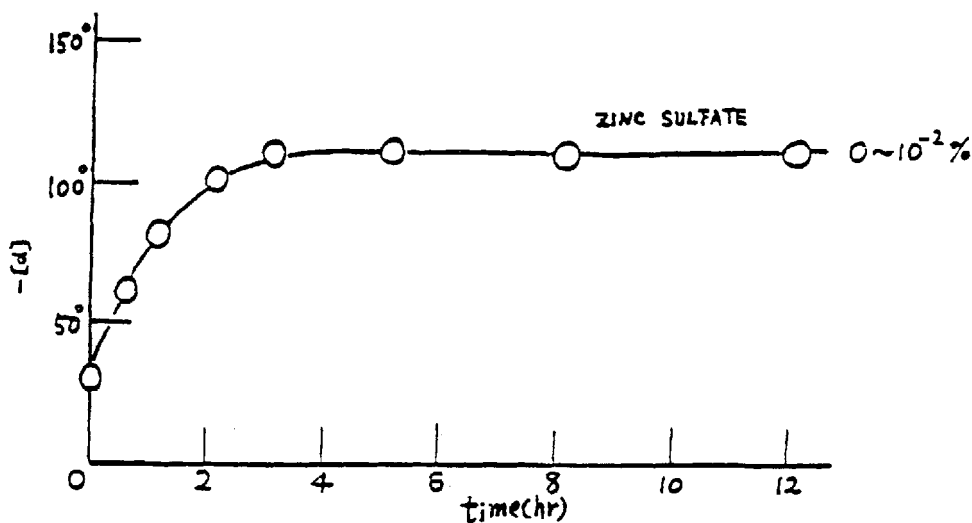


FIG. 12. Specific rotation vs time of 2% albumin in 7 M urea, 10^3 R, and 30° C in the presence and in the absence of zinc sulfate.

the values of the final specific rotation and the percentage of salt of the alkaline-earth metal or of the control metal are shown in Figs. 13-24.

In the presence of the salt of an alkaline-earth metal, the specific rotations of albumin solutions are described in a linear fashion by adapting a logarithmic abscissa for the concentration of the salt of an alkaline-earth metal (in %) as shown in Figs. 13-16.

In the presence of the salt of a control metal, the specific rotations of albumin solutions did not decrease (Figs. 17-24).

From these results it is clear that the effect of the salt of an alkaline-earth metal on the optical rotation is apparently related its protective action on the changes in the internal relationships of the atoms in protein molecule.

DISCUSSION

As stated above, it is well known that some alkaline-earth metals, such as calcium interact with some biological macromolecules, such as protein [1], and also protect the changes of permeability of some

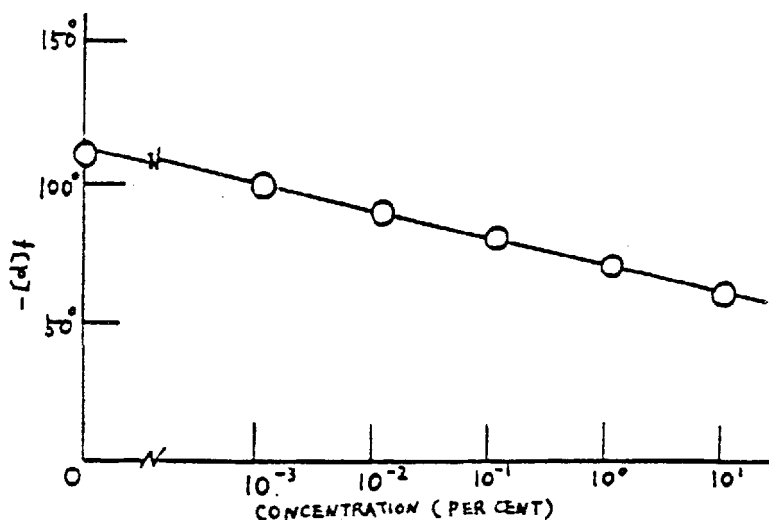
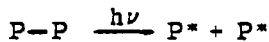


FIG. 13. Dependence of the protective effect on the concentration of magnesium chloride; 2% albumin in 7 M urea, 10⁵ R, and 30 °C.

biological macromolecular membrane, such as cell membranes, induced by radiation [2, 3].

Changes in the internal relationships of the atoms in protein molecule are estimated from the changes in optical rotation as shown in Figs. 1-12. The relationship between the change in optical rotation and the concentration of the salt of an alkaline-earth metal is related to the change in the internal relationships of the atoms in protein molecule and to their inhibition. When the concentrations of protein and urea and the radiation dose are all constant, a change in the concentration of salt of an alkaline-earth metal results in a change in optical rotation required for the internal relationships of the atoms in protein molecule; see Figs. 13-16. This behavior closely resembles that found with amino acids, as shown by a similar dependence on the concentration [5]. The change in the internal relationships of the atoms in protein molecule by γ -radiation may be shown by a change in the optical rotation. The activated group in the vicinity of the asymmetric carbon atom in protein molecule by γ -radiation may be detected by a change in the optical rotation [4]. Activated groups may be formed as a direct result of γ -radiation:



It may be that the groups activated in protein molecule by γ -radiation

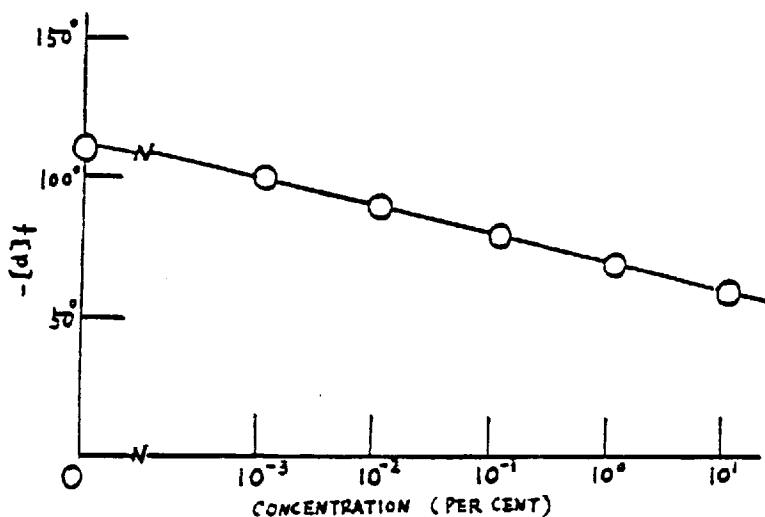


FIG. 14. Dependence of the protective effect on the concentration of calcium chloride: 2% albumin in 7 M urea, 10³R, and 30°C.

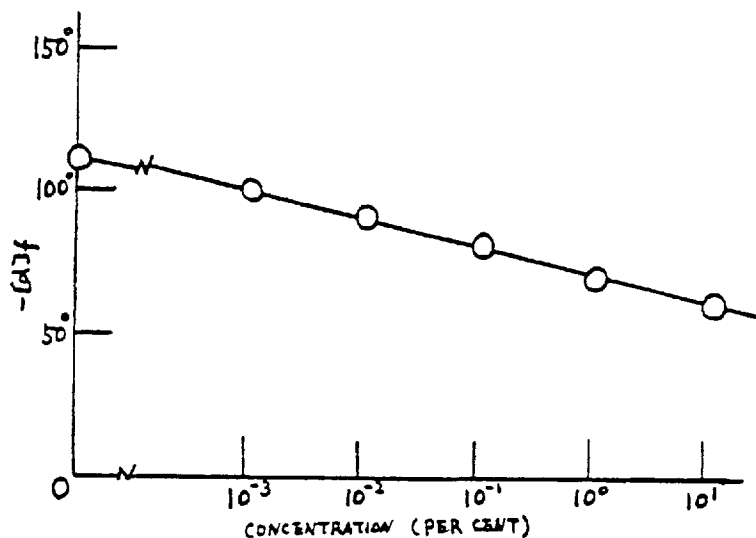


FIG. 15. Dependence of the protective effect on the concentration of strontium nitrate; 2% albumin in 7 M urea, 10^3 R, and 30° C.

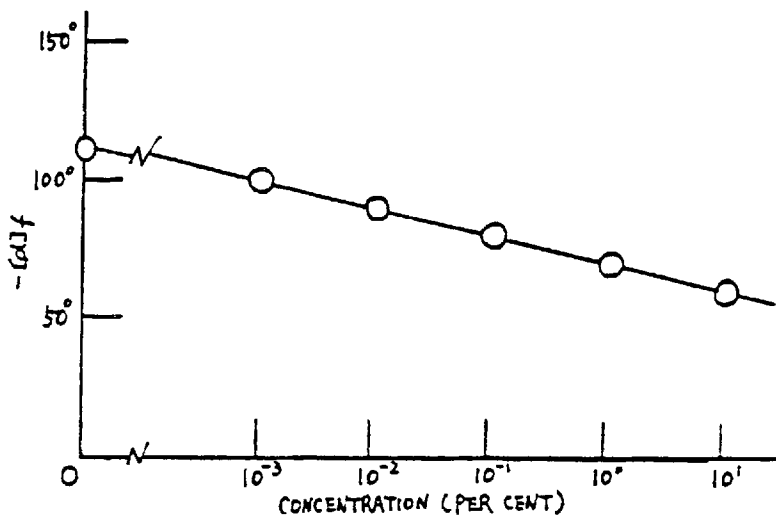


FIG. 16. Dependence of the protective effect on the concentration of barium chloride; 2% albumin in 7 M urea, 10^3 R, and 30° C.

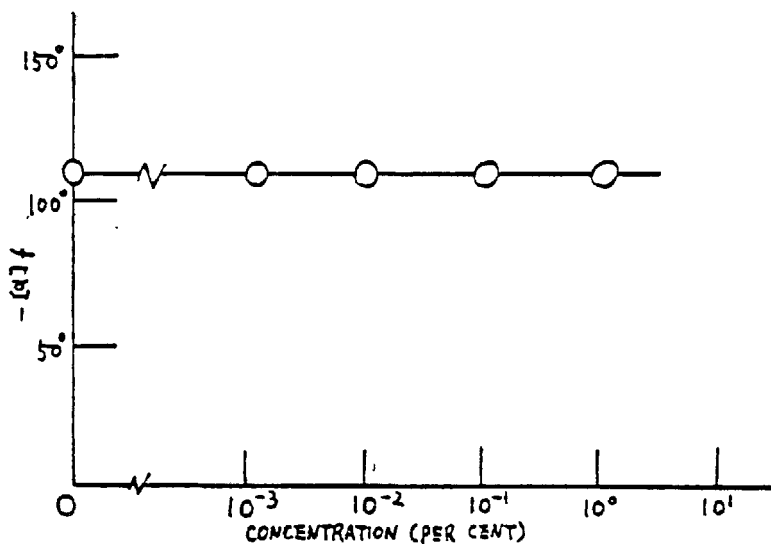


FIG. 17. Dependence of the protective effect on the concentration of lithium chloride; 2% albumin in 7 M urea, 10^3 R, and 30° C.

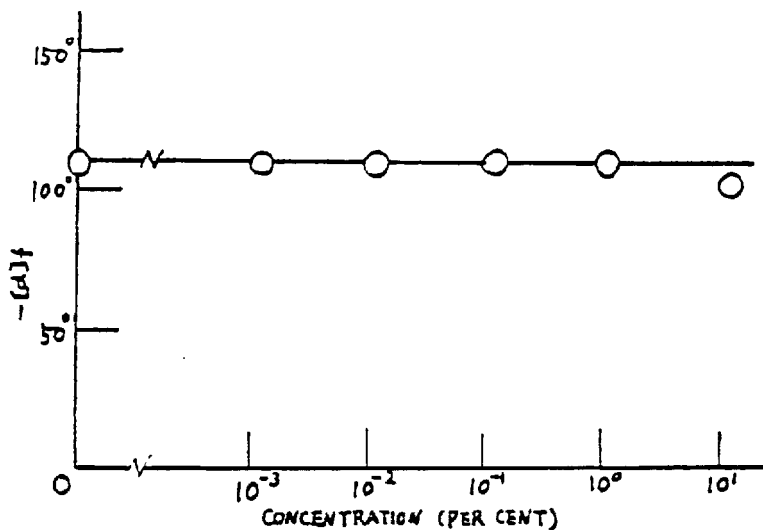


FIG. 18. Dependence of the protective effect on the concentration of sodium chloride; 2% albumin in 7 M urea, 10^3 R, and 30° C.

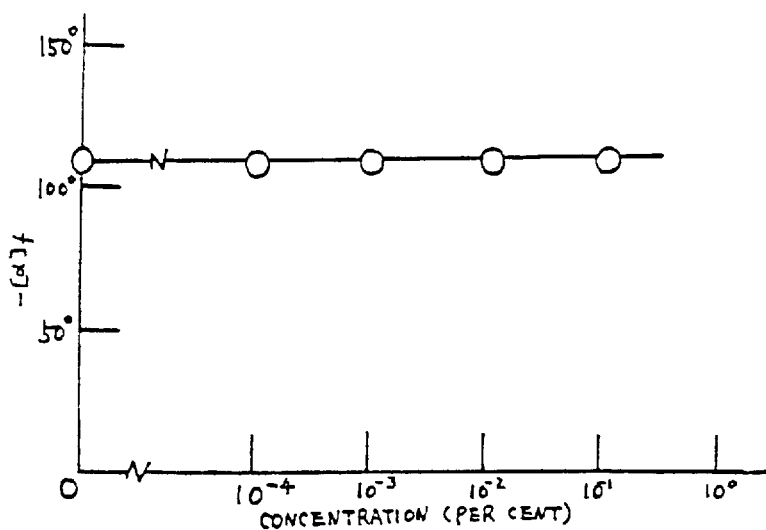


FIG. 19. Dependence of the protective effect on the concentration of potassium nitrate: 2% albumin in 7 M urea, 10^3 R, and 30° C.

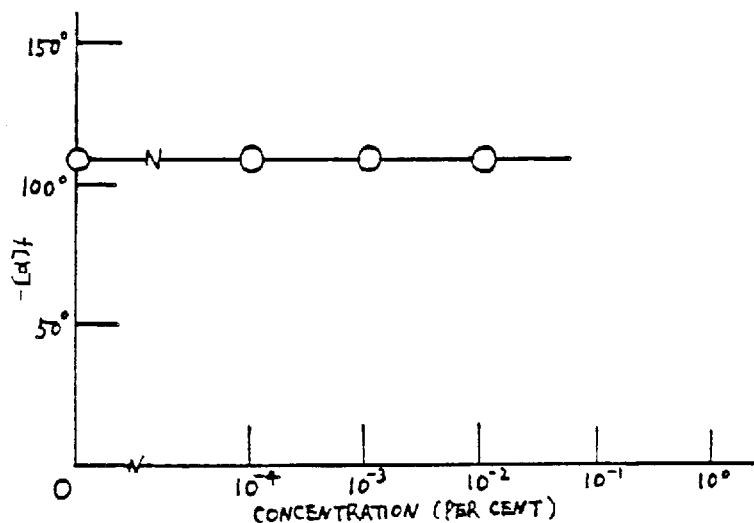


FIG. 20. Dependence of the protective effect on the concentration of ferrous chloride; 2% albumin in 7 M urea, 10^3 R, and 30° C.

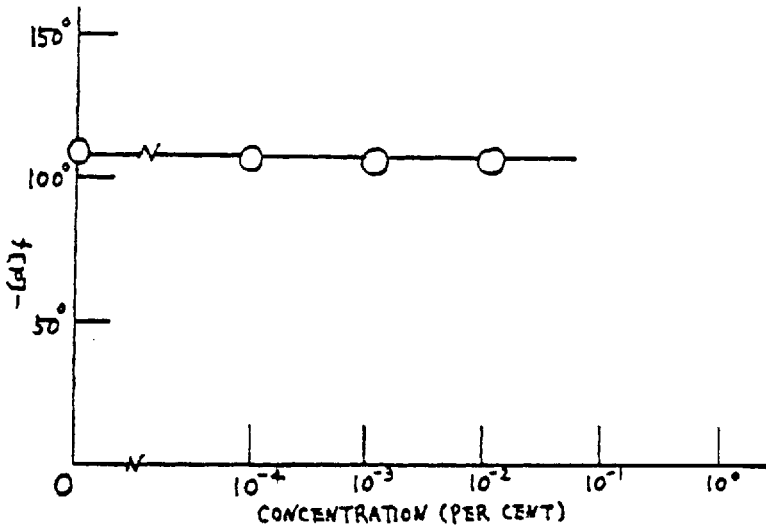


FIG. 21. Dependence of the protective effect on the concentration of ferric nitrate; 2% albumin in 7 M urea, $10^3 R$, and 30° C.

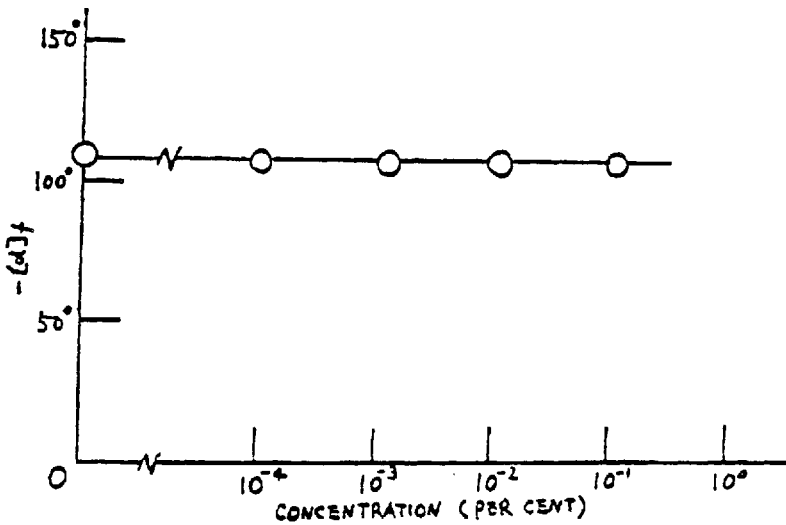


FIG. 22. Dependence of the protective effect on the concentration of nickel sulfate; 2% albumin in 7 M urea, $10^3 R$, and 30° C.

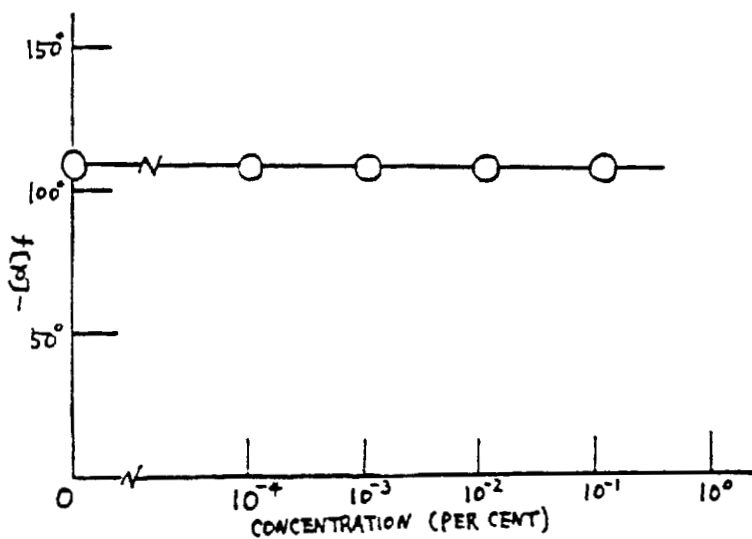


FIG. 23. Dependence of the protective effect on the concentration of aluminum nitrate; 2% albumin in 7 M urea, 10^3 R, and 30°C.

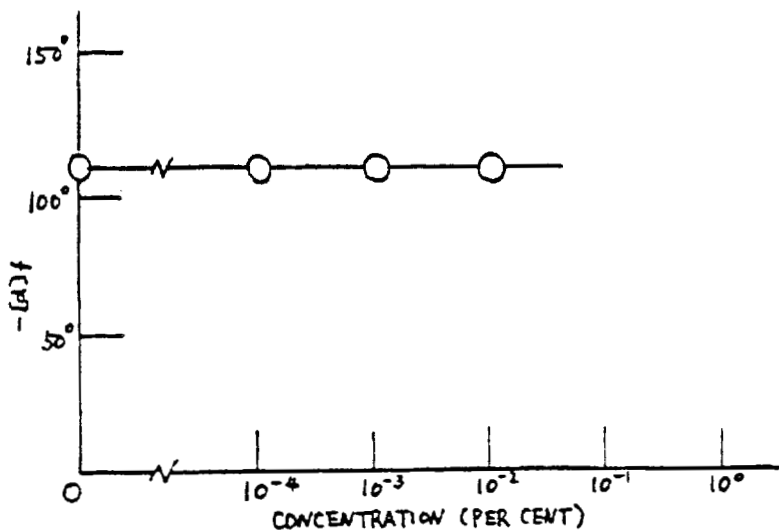


FIG. 24. Dependence of the protective effect on the concentration of zinc sulfate; 2% albumin in 7 M urea, 10^3 R, and 30°C.

could be moderated by the protective action of an alkaline-earth metal after irradiation, thereby reducing the number of activated groups formed in protein molecule before a change in the internal relationships of the atoms can occur. Since an increase in the concentration of the salt of an alkaline-earth metal (in %) decreases the change in specific rotation of a protein, protection against change of the internal relationships of the atoms in protein molecule as caused by γ -radiation must be due to the presence of the salt of the alkaline-earth metal. At the concentration studied, the protection may be due to the interaction of the alkaline-earth metal with the activated groups before they can attack the urea or interact with other groups in the protein molecules. The process assumed for the protective reaction was



where P-P is the group in the initial position in the vicinity of the asymmetric carbon, P* is the activated group, S is the alkaline-earth metal, and P-S-P is the alkaline-earth metal group in the protein linkage.

For the present system, the observed specific rotation is expressed in linear fashion by adapting a logarithmic abscissa for the concentration of the salt of the alkaline-earth metal in percent;

$$[\alpha]f = b - a \log X$$

This formula agrees with the experimental data plotted in Figs. 13-16.

The alkaline-earth metal ion may be bound at the imidazole, carboxyl groups, or peptide O,N of protein molecule, and they protect against changes in the internal relationships of the atoms in the protein molecule from the radiation damage.

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