



Valency Stabilization of Polyvalent Ions During Gamma Irradiation of their Aqueous Solutions by Sacrificial Protection

I - Valency Stabilization of Fe(II) Ions by sulphite Ions

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ملخص

تظهر الأيونات الفلزية متعددة التكافؤ حساسية كبيرة عند تشعيع محاليلها المائية بأشعة جاما .
والدراسة المعروضة هي جزء من دراسة شاملة تتعلق بتثبيت أو حماية تكافؤات بعينها لبعض الأيونات متعددة التكافؤ أثناء تعريض محاليلها المائية لإشعاعات جاما .
وقد تم في هذا البحث دراسة تصرف أيونات الحديد الثنائي في المحاليل المائية الحامضية أثناء تشعيعها بأشعة جاما في وجود أيونات الكبريتيت وذلك بهدف تفهم ميكانيكية عملية الحماية التي يضيفها وجود أيونات الكبريتيت في المحاليل على أيونات الحديد الثنائية. وقد تم تحديد ظروف وحدود عملية تثبيت التكافؤ التي حدثت .

Abstract

Polyvalent ions are very sensitive to gamma irradiation in aqueous solutions. The present work is a part of a more comprehensive study dealing with the stabilization of protection of certain oxidation states of some polyvalent ions during their gamma irradiation in aqueous systems. The behaviour of aqueous Fe(II) solutions during gamma irradiation, in presence of sulphite ions has been studied in details in order to understand the prevailing protection mechanism. The conditions and stabilization limits in the studied case has been found out.

1 - INTRODUCTION

Polyvalent ions in aqueous solutions are very sensitive to the effect of gamma radiations. In some practical applications, separation of certain polyvalent ions depends largely on the availability of a certain oxidation state of the ionic species. This indicates that the stabilization of certain oxidation states of certain ions, when present in a strong irradiation field, is an important problem in applied radiation chemistry.

Protective effects induced by traces of some chemicals against X- or gamma radiations have been known since a long time^(1,2,3,4). In its broadest sense, the term protection in radiation chemistry has a variety of meanings dependent on the view point of the observer as well as the details of the process investigated. For example, if :



and both R and X react with a second species N and thus modify or destroy it, an active agent may be added with the objective of intercepting or scavenging the radicals before they can enter into the reaction with N. In this way N is protected from chemical action but it is not protected from decomposition⁽⁵⁾. It should be pointed out that protection on radiolytic systems is a phenomenon that is greatly related to competitive reactions.

Competition depends on the equilibrium constant of the prevailing reactions and also on the redox potentials of reactions in aqueous systems particularly when polyvalent ions are involved.

Upon irradiating 1 millimolar ferrous ions solution in 0.08 N H₂SO₄ with gamma radiations, iron ions were completely oxidised within two hours when the gamma dose rate was 310 Gy/h. This has been attributed to the action of radicals resulting from water radiolysis. When sulphite ions were introduced in such a system the valency of the iron ions was stabilized for extended periods of time depending on the concentration of the sulphite ions used.

The present work is part of a more comprehensive study dealing with the protective effect exerted by some chemicals on some polyvalent ions solutions under different gamma irradiation conditions. Thus, Fe(II) ions in slightly acidic solutions, which normally are rapidly oxidized during gamma irradiation, were irradiated under different conditions in presence of Na₂SO₃, used as a protective agent for the ferrous ions. The nature of the valency stabilization processes in the studied systems have been investigated aiming to throw some light on the nature of the competitive reactions occurring in such systems.

2 - EXPERIMENTAL

2.1 -Chemicals

Analytical grade ferrous sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), ferric sulphate ($\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$), Sodium sulphite ($\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$) and Sulphuric acid (98%) Sp.Gr.1.84 were used. Double distilled water was used all over the work.

2.2 - Preparation of solutions

Ferrous sulphate crystals were washed twice with double distilled water followed by A.R.Acetone and then dried by heating at 50°C for few minutes. A stock 10^{-2}N Fe (II) solution in $0.8 \text{ N H}_2\text{SO}_4$ was prepared by dissolving an accurately weighed amount of ferrous sulphate in about 400 ml freshly boiled and cooled bidistilled water to which was added 22 ml Conc. H_2SO_4 . The solution was then completed double distilled water to the mark in a 1 Litre volumetric flask. The exact concentration of Fe(II) in solution was determined potentiometrically using a standard potassium permanganate solution⁽⁶⁾.

A stock 10^{-2}M Fe (III) solution was prepared by dissolving the necessary amount of A.R. $\text{Fe}_2(\text{SO}_4)_3$ in about 400 ml hot bidistilled water to which were added 22 ml conc. sulphuric acid. The cold solution was completed to the mark in a 1 litre volumetric flask. The exact concentration of Fe(III) was titrimetrically determined against a standard EDTA solution using Tiron indicator at $40\text{-}50^\circ\text{C}$ and after adjusting the pH of the solution at about 2.5⁽⁷⁾.

Sodium sulphite solutions, exactly about 0.1 M, were prepared by dissolving the calculated amount of A.R. $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$ in freshly boiled and cooled double distilled water and the solution completed to the mark in a volumetric flask. The exact concentration of SO_3^{2-} was determined titrimetrically after adding a known excess of a standard iodine solution and determining the excess iodine with a standard $\text{Na}_2\text{S}_2\text{O}_3$ solution using starch indicator⁽⁸⁾.

2.3 - Preparation of irradiated samples

All irradiated liquid samples were irradiated using 50 ml capacity irradiation glass tubes, 15 cm in hight, and 2.5 cm in diameter and provided with a glass stopeered neck 1 cm in diameter.

The irradiated samples were always prepared by adding the appropriate amounts of standard sodium sulphite solution to a solution

prepared by adding water to 5 ml of the stock 10^{-2}N Fe (II) or 10^{-2}N Fe(III) in 0.8 N H_2SO_4 and the mixtures were quantitatively transferred and completed to the mark in 50 ml volumetric flasks. The solutions were then introduced in the glass stoppered irradiation tubes and irradiated.

At certain intervals, samples were removed from the irradiation field and analysed.

2.4 - Irradiation

Samples were irradiated in a Canadian ^{60}Co Gamma cell-220 which was calibrated by the Fricke dosimeter,⁽⁹⁾.

2.5 - Analysis of the irradiated samples

a - Determination of iron ions in irradiated or unirradiated solutions:

Fe(II) concentration in solution have been determined spectrophotometrically by measuring the absorbance of the orange red complex formed with 1,10- Phenanthroline. The absorbance of the analysed solution was always measured against a reagent blank at 510 nm. The molar absorptivity is 1.16×10^4 at λ_{max} ,⁽¹⁰⁾.

Fe(III) concentration in solution have been measured spectrophotometrically within the range 250-360 nm with a maximum absorption at 305nm. The molar absorptivity is 2310 which is in good agreement with the value cited in literature.

The unknown concentrations of iron samples were determined by calibration curves constructed within the concentration range 1.0×10^{-5} - 1.5×10^{-4} M for Fe(II) solutions and 5×10^{-5} - 4.5×10^{-4} M in case of Fe(III) solutions.

b - Determination of sulphite ions :

The concentration of SO_3^{2-} in the stock sulphite solution and in the irradiated samples was determined titrimetrically by adding a known excess of a standard iodine solution and determining the excess iodine by a standard thiosulphate solution using starch as indicator⁽⁸⁾.

3. RESULTS AND DISCUSSIONS

In the present work, the possibility of protecting ferrous ions by sulphite ions was investigated. The standard oxidation potentials of Fe(II) and SO_3^{2-} are -0.77v and - 0.17 v respectively. This could probably

indicate the possibility of using sulphite ions under strictly specified conditions to act as a protective agent for Fe(II) solutions during gamma radiolysis.

The stability of sulphite ions was investigated in neutral and slightly acidic solutions with sulphuric acid concentrations ranging from 0.05 to 0.4 N. The results obtained are shown graphically in figure 1. From these results it could be observed that sulphite ions in neutral solutions are very unstable in such a way that a 10^{-2} N solution completely decomposed in 20 hours. Sulphite solutions showed a much larger stability in dilute sulphuric acid media within the concentration range 0.05-0.2 N. At more higher acidic concentrations e.g. at 0.4 N H_2SO_4 the sulphite ions stability markedly degraded. Consequently, in further experiments sulphite ions were used as a protective agent in 0.08 N sulphuric acid.

The effect of Fe (II) on the stability of sulphite ions was also studied. Thus, the concentration of SO_3^{2-} ions was followed in a series of solutions containing increasing amounts of sulphite ions in 0.08 N H_2SO_4 and also in another series of solutions containing, in addition, 10^{-3} N Fe(II) ions. The results obtained are shown in figure 2. From these results it could be observed that in presence of Fe (II) ions sulphite ions degraded more rapidly. It could be also observed that during the gradual decay of the sulphite ions Fe (II) concentration remained constant as long as the sulphite ions were still existing in the medium, after that a steady state was reached when about 50% of the Fe (II) ions were oxidized to Fe(III) ions. On increasing the SO_3^{2-} ions concentration keeping the Fe(II) constant the stability time of the iron ions was consequently increased.

Fe (II) ions are known to be rapidly oxidised in gamma irradiated acidic solutions. Figure 3 shows that a 10^{-3} N Fe (II) acidic solution was completely oxidised in about two hours upon using a gamma dose rate of 310.2 Gy/h .

The protective effect of sulphite ions exerted on ferrous ions when both were subjected to gamma irradiation has been studied by adding increasing amounts of sulphite ions to a certain concentration of Fe (II) ions (10^{-3} N) in 0.08 N H_2SO_4 . The concentration of Fe (II) ions was followed during the continued irradiation of the system. The results obtained are shown in figure 4. From these results it could be observed that sulphite ions in the irradiated systems protected the Fe (II) ions against radiolytic oxidation and the protection time was proportional to the concentration of the sulphite ions used. The protection capacity of

sulphite ions was revealed by plotting the sulphite ion concentration against the corresponding protection time. The results are shown in figure 5; which reveals that the protection time increased linearly with sulphite concentration used. The behaviour of sulphite ions during the protection period was studied by following the decay of SO_3^{2-} ions in presence and absence of Fe (II) during gamma irradiation of the system. The results obtained are shown in figure 6 which shows that the decay of SO_3^{2-} ions in presence and absence of Fe (II) ions occurs at the same rate during radiolysis. From the data given in figures 5 and 6 it could be noted that the time during which ferrous ions were protected by sulphite ions was almost equal to the complete decay time of sulphite ions, both being superimposed in figure 7.

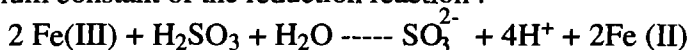
It is therefore evident that SO_3^{2-} ions exerted a protective effect on Fe(II) when both ionic species were mutually irradiated.

In order to try to identify the prevailing mechanism it has been found necessary to study, the interaction process occurring between Fe (III) and SO_3^{2-} ions .

Thus, Fe (III) ions in 0.08 N H_2SO_4 were kept in contact with a known excess of SO_3^{2-} (0.022N Na_2SO_3). The concentrations of both the Fe (II) formed and residual SO_3^{2-} were determined at intervals. The results are represented graphically in Fig. (8) .

From these data it could be observed that Fe (III) ions reduction occurred gradually at a higher rate at first, then the rate of reduction gradually decreased. Complete reduction of a 10^{-3} M Fe (III) ions into Fe (II) occurred in about 3 hours on using 22 times excess of SO_3^{2-} . After the complete reduction of Fe (III) within 3 hours, the Fe (II) ions formed remained stable as long as SO_3^{2-} were still remaining in the medium. After the complete decay of SO_3^{2-} the Fe(II) started to decay until the concentration of Fe(II) was reduced to about half of the initially used amounts.

Referring to the normal reduction potentials of SO_3^{2-} and Fe (III) the equilibrium constant of the reduction reaction :



is equal to 2.19×10^{20} which indicates that the reduction reaction is in principle feasible but is a rather slow reaction.

This shows that the protection of Fe (II) ions by SO_3^{2-} most probably goes by the interaction of SO_3^{2-} with the oxidizing species formed in solution upon radiolysis thus protecting the existing Fe (II) ions. Moreover, from the previous discussions, it is possible to conclude

that the protective effect of sulphite ions starts at the very beginning of mutual irradiation.

In order to get a more elaborate idea about the mechanism of the protective effect of SO_3^{2-} during γ -radiolysis of Fe (II) solutions, the effect of SO_3^{2-} ions has been studied during irradiation of Fe (III) solutions. The results obtained are represented graphically in Fig. (9). From these data it could be observed that upon γ -irradiation of the mixture containing Fe (III) and 22 fold excess of SO_3^{2-} ions, Fe (III) ions were completely reduced within 2-3 hours. The formed Fe (II) ions remained stable as long as SO_3^{2-} existed in the medium. Then after the complete exhaustion of SO_3^{2-} the Fe (II) ions were rapidly completely oxidized.

Comparing the results in Fig. (9) with those in Fig. (4) for the Fe(II) ions behaviour, it is possible again to conclude that the protection of Fe (II) occurs by the direct interaction of SO_3^{2-} with the oxidizing species in the irradiated systems.

Referring to the rate constant of the OH radical reaction with Fe(II) ($1.3 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) and that of OH radical reaction with SO_3^{2-} ($5.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) or with HSO_3^- ($9.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$)⁽¹¹⁾. It is clear that in presence of excess SO_3^{2-} ions the oxidising OH radicals will very probably interact with SO_3^{2-} to a greater extent. This preferential interaction leads to the observed protective effect of sulphite on Fe (II).

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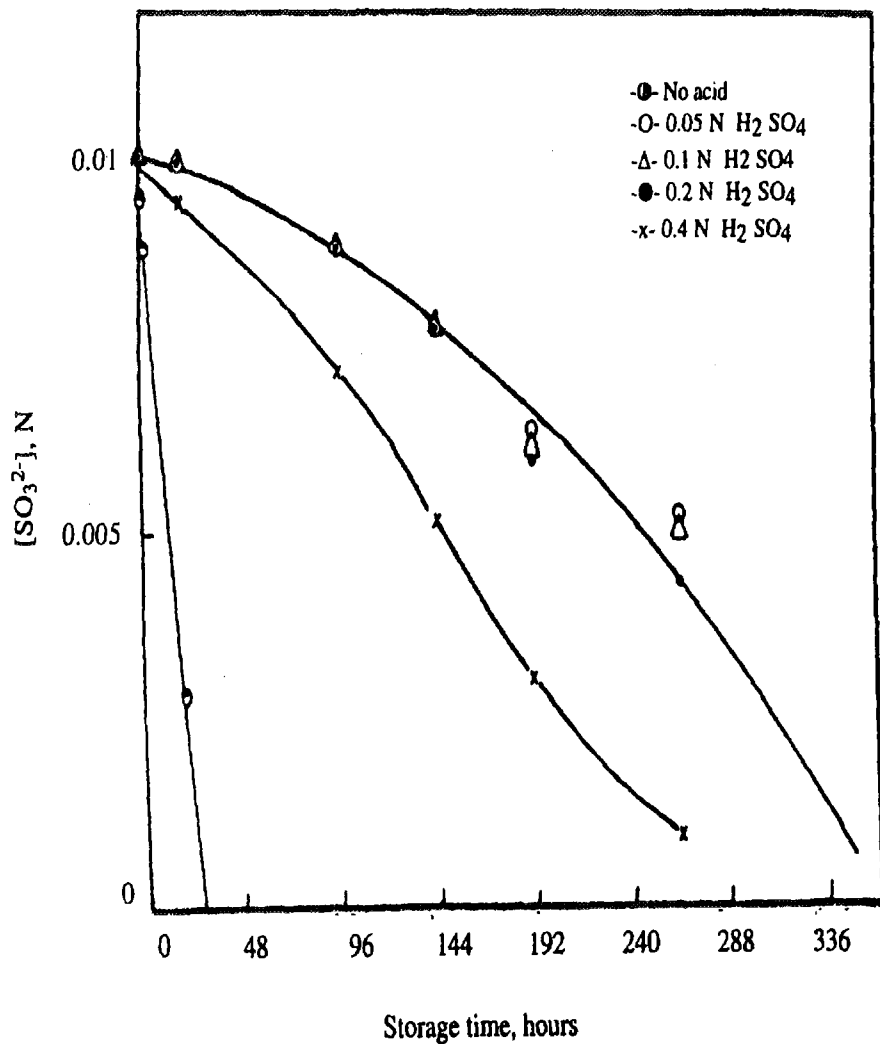


Fig. (1): Stability of aqueous and slightly acidic sodium sulphite solutions with time.

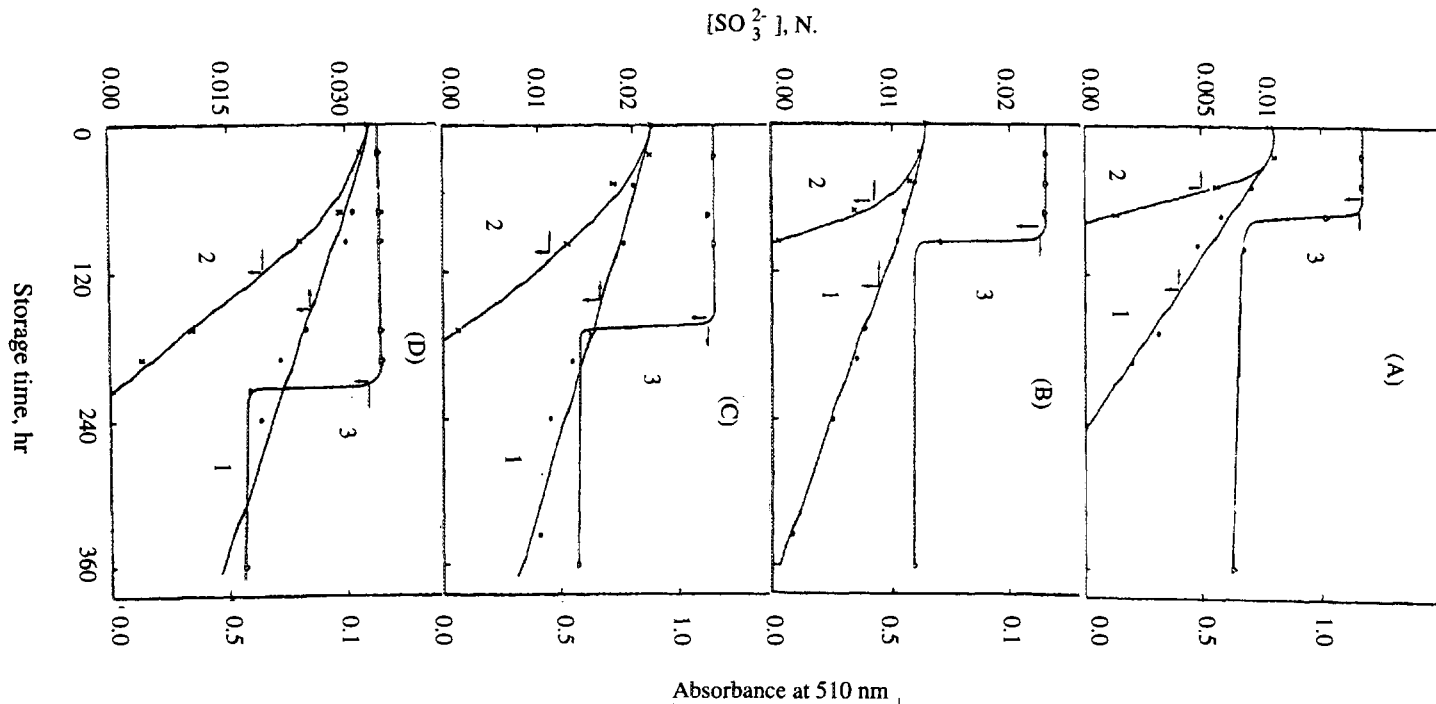


Fig.(2): 1 - Stability of SO₃²⁻ in different pure sulphite solutions (0.0078 N (A), 0.013N (B), 0.022 N (C) and 0.033 N (D)) with time
 2 & 3 - Stability of SO₃²⁻ and Fe (II) ions in similar SO₃²⁻ solutions containing 10⁻³ N Fe (II) ions.

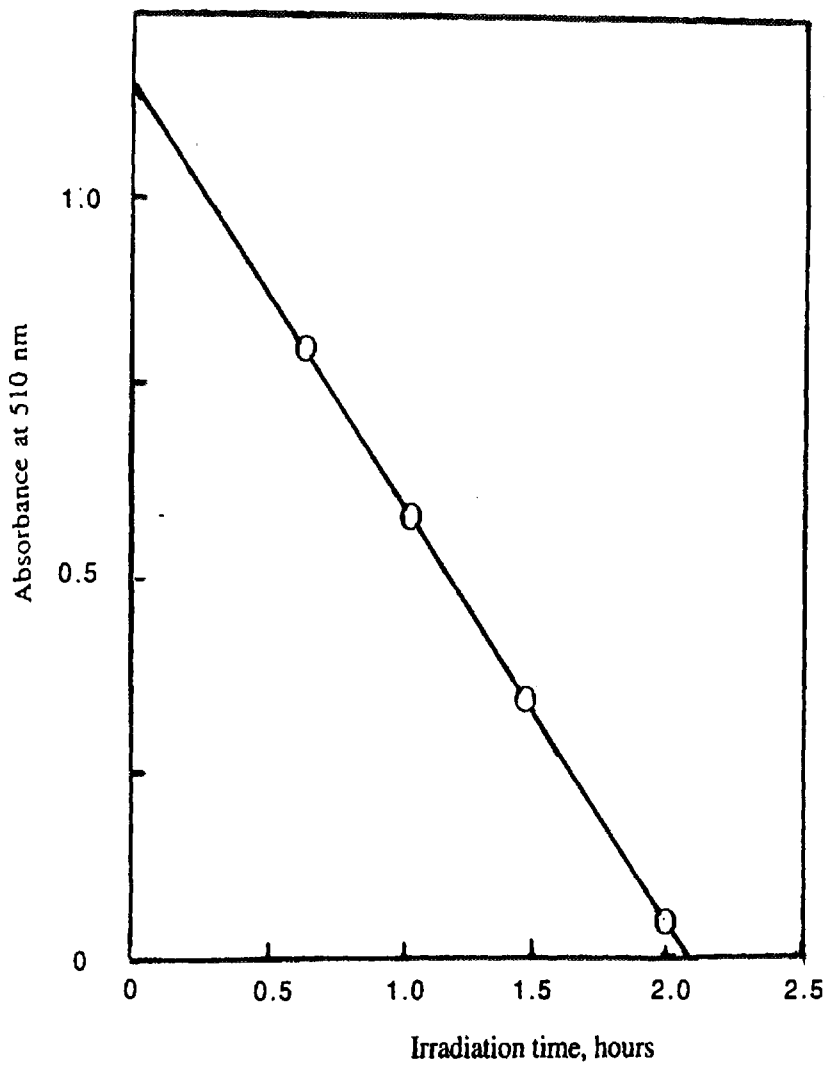


Fig. (3): Radiolytic decay of 10^{-3}N Fe (II) solution in presence of $0.08\text{ N H}_2\text{SO}_4$. (γ - dose rate = 310.2 Gy/hr).

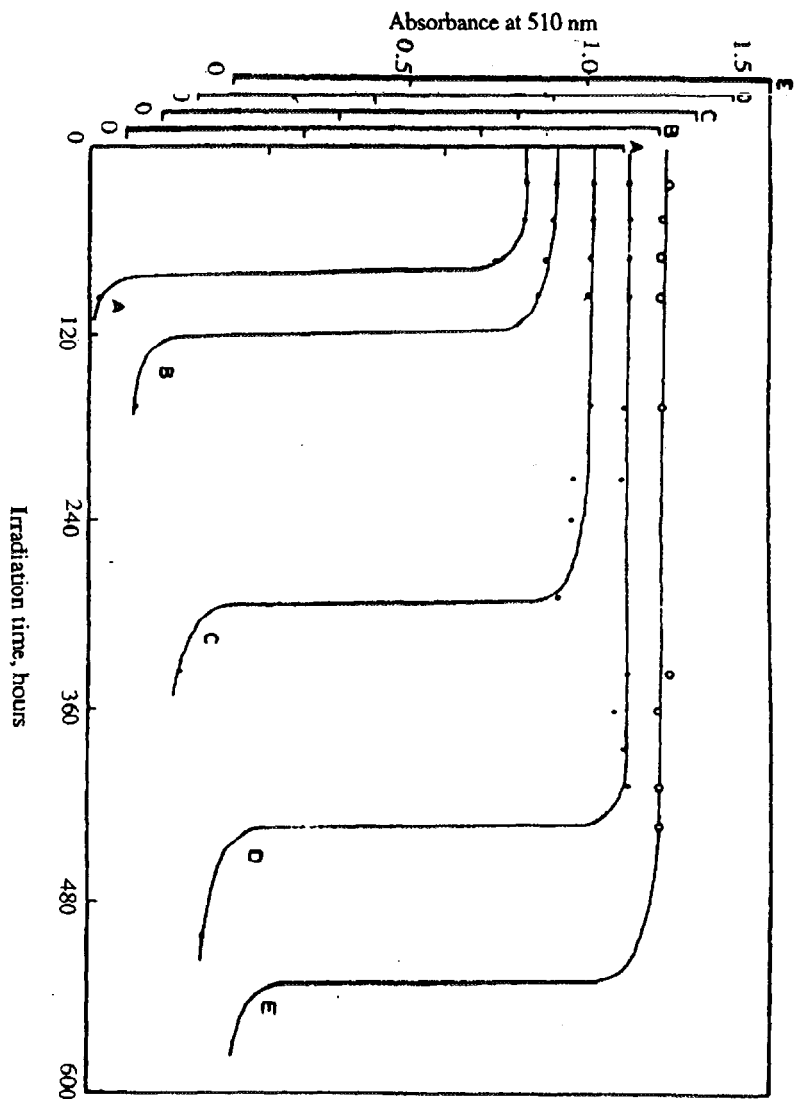


Fig. (4): Stability of 10^{-3} N Fe (II) ions in presence of various concentrations of sulphite during γ -irradiation (Initial dose rate = 316.5 Gy/hr.)
 $[\text{SO}_3^{2-}]$: A = 0.9×10^{-2} N; B = 1.5×10^{-2} N; C = 3×10^{-2} N;
D = 4.5×10^{-2} N; E = 6×10^{-2} N.
 $[\text{Fe (II)}]$: 10^{-3} N.

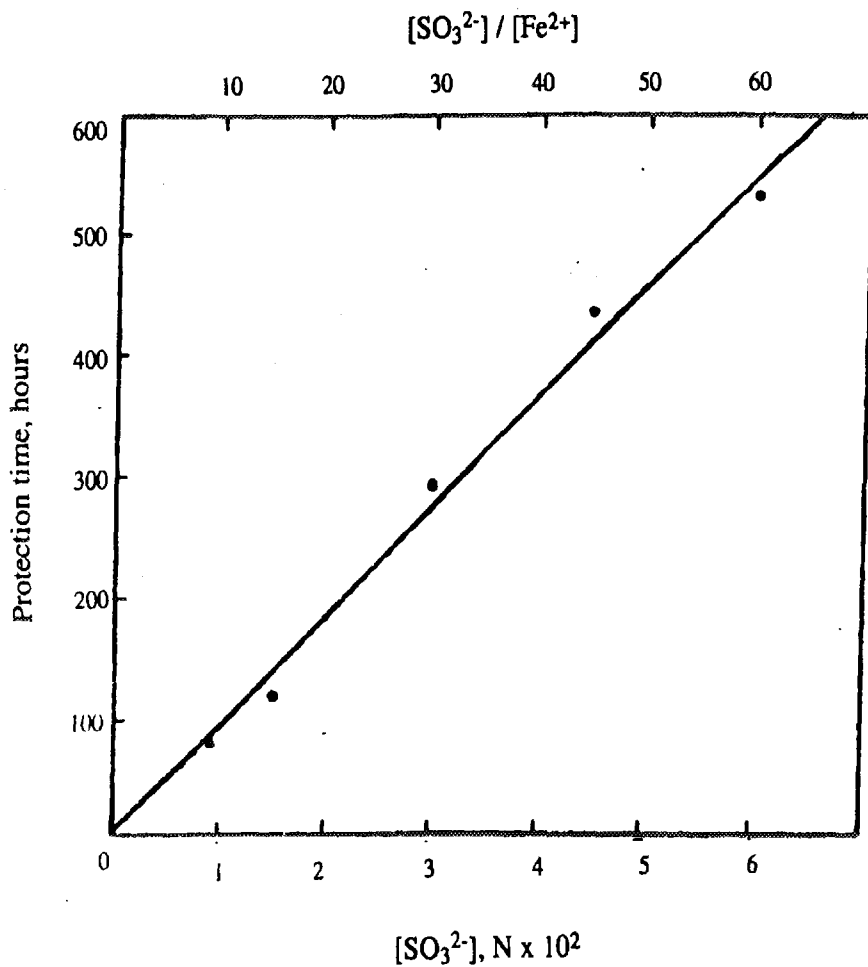


Fig. (5): Protection time of SO_3^{2-} ions in γ -irradiated 10^{-3} N Fe (II) solution containing various concentrations of SO_3^{2-} ions. (Initial dose rate = 316.5 Gy/hr.)

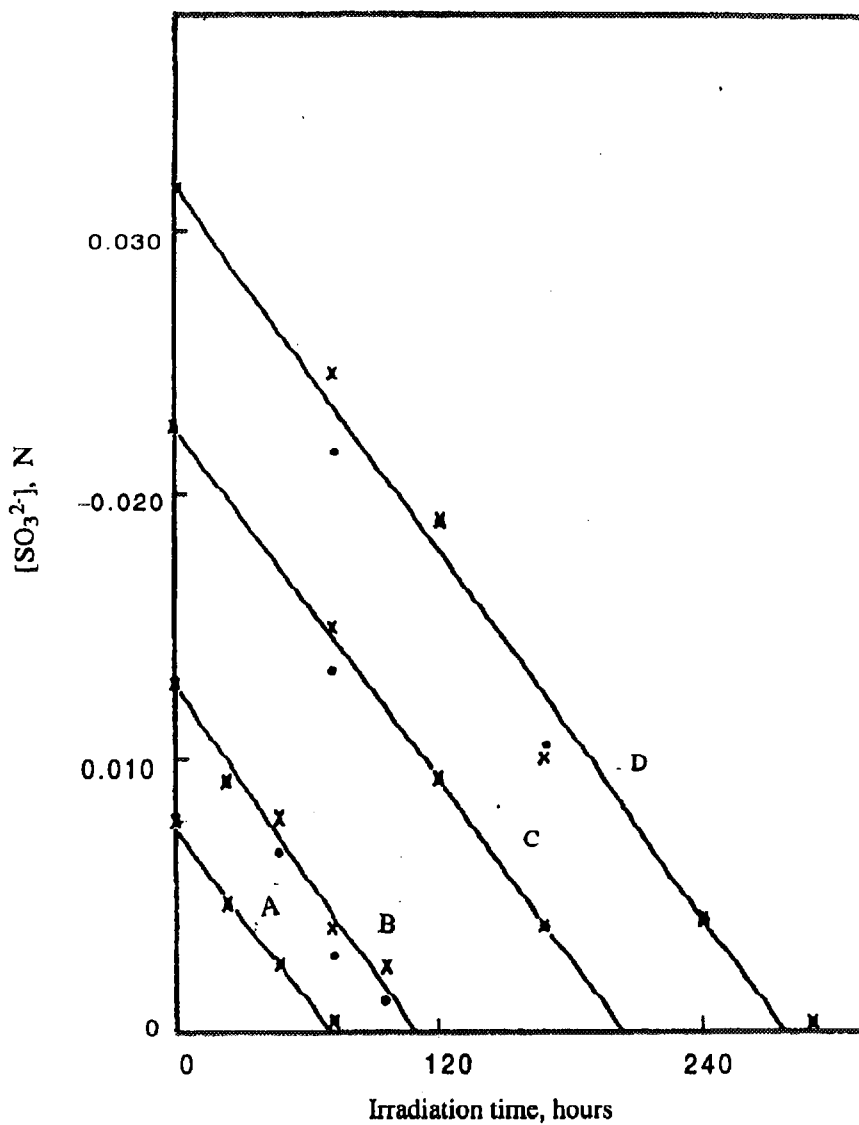


Fig. (6): Decay of SO_3^{2-} in presence and absence of 10^{-3} N Fe (II) ions in 0.08 N H_2SO_4 during γ -Irradiation.

-x- In presence of Fe (II), -•- In absence of Fe (II).

$[\text{SO}_3^{2-}]$: A = 0.78×10^{-2} N; B = 1.3×10^{-2} N; C = 2.26×10^{-2} N; D = 3.16×10^{-2} N.

(Initial dose rate = 316.5 Gy/hr.)

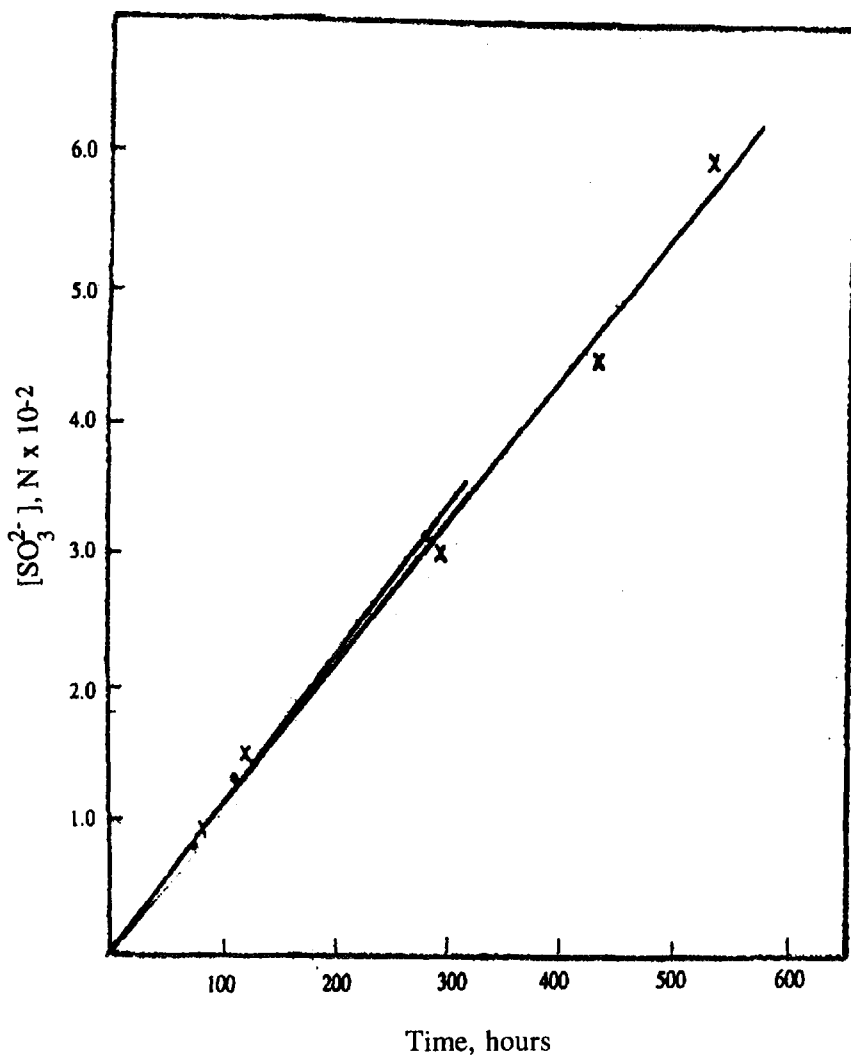


Fig. (7): Complete decay time of SO_3^{2-} upon γ -Irradiation
 (●) (from Fig. 6) as related to the protection time of $10^{-3}N$
 Fe (II) in presence of various concentrations of SO_3^{2-} (x)
 (from Fig. 5).

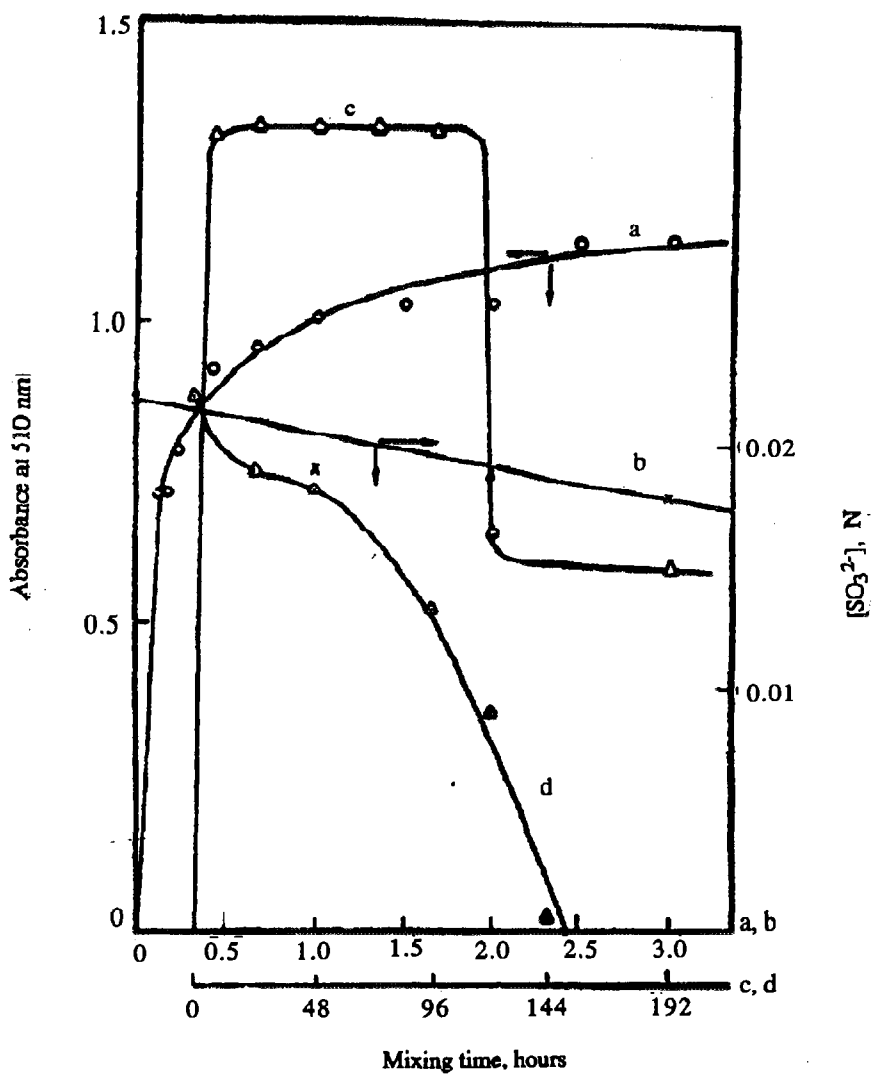


Fig. (8): Reduction Kinetics of Fe (III) ions by SO_3^{2-} ions
 a- Formation of Fe (II) with time in 10^{-3} N Fe (III) solution
 b- Decay of 0.022 N SO_3^{2-} ions in presence of 10^{-3} N Fe (III)
 c- Change of $[\text{Fe}^{2+}]$ with time in 1.2×10^{-3} N Fe(III) solution
 d- Decay of 0.0022 N SO_3^{2-} ions in presence of 1.2×10^{-3} N Fe (III).

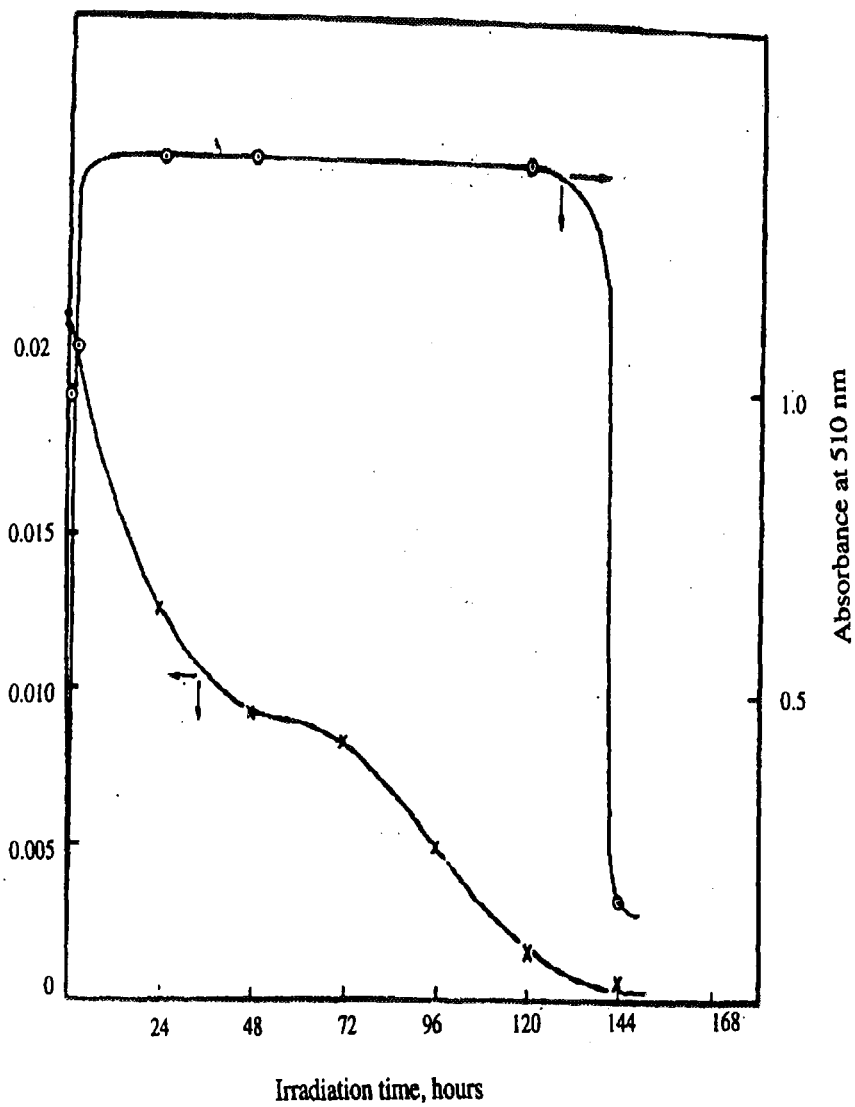


Fig. (9): Behaviour of Fe^{3+} ions during γ -irradiation in presence of $0.022 \text{ N SO}_3^{2-}$ ions.