Radiolysis of Co^{III}-EDTA Solution by Charged Particles through $^6Li(n,\alpha)^3H$ Reaction

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This experiment was to study the radiolysis of Co^{II}-EDTA solution in 0.8N H_2SO_4 saturated with air by charged particles produced through $^6Li(n,\alpha)^3H$ reaction. The experimental results show that the G(-Co^{II}-EDTA) decreases as the absorbed dose rate increases. For the same absorbed dose rate, the values of G(-Co^{II}-EDTA) are practically independent of absorbed dose. The effects of concentration and temperature are also studied.

Key Words: radiolysis, Co^{II}-ethylenediamine tetraacetic acid solution, $^6Li(n,\alpha)^3H$ reaction, spectrophotometry

1. Introduction

Several reports have dealt with the radiolysis of Co^{II}-EDTA solution[1)~4)]. One of the authors has studied the feasibility of its applications to chemical dosimetry[5),6)]. However, these reports and studies are confined to the radiolysis due to γ-rays only. The reports dealing with radiolysis by charged particles are scarce. It is the objective of this work to fill the gap.

The charged particles produced through $^6Li(n,\alpha)^3H$ reaction have 4.78 MeV and the reaction cross section is 945 b for neutron; the dose rate of the charged particles as a result of ^6Li present in the solution can be calculated as follows:

$$D=\frac{4.78\times1.6\times10^{-6}\times3600}{100}\times\frac{n\sigma\phi}{\rho} \quad (1)$$

where

n: No. of ^6Li nuclei per milliliter solution
ϕ: thermal neutron flux ($n\cdot cm^{-2}\cdot s^{-1}$)
σ: cross section of ^6Li in (n,α) reactor(b)
ρ: density of solution ($g\cdot cm^{-3}$)
4.78: energy of charged particles (MeV)
1.6×10^{-6}: erg per MeV
3600: sec per hour
100: erg per rad.

2. Experimental

2·1 Material

The distilled water used was the sub-boiling water. This type of distilled water was prepared by distillation of deionized water followed by another distillation under the sub-boiling condition. The reagent Na(Co^{II}-EDTA)·$3H_2O$ was synthesized according to Young's direction[5)]. The ^6Li-enriched Li_2CO_3 was obtained from Oak Ridge National Laboratory(ORNL). It contains 95.68% of ^6Li, and was dissolved in H_2SO_4 to make a concentration of 0.8N. The PE tubes for neutron irradiation are 0.8 mm thick with 15 mm ID. All chemicals used were of reagent grade.

Na(Co^{II}-EDTA)·$3H_2O$ was dissolved in 0.8N H_2SO_4 saturated with air and different amounts of ^6Li were added to make solution with various ^6Li contents. An aliquot of each 3 ml was pipetted into a PE tube containing ^6Li, and 3 ml of the similar solution with no ^6Li added was pipetted into another PE tube. After being sealed, both tubes were irradiated at the 1 MW Tsing Hua Open-pool reactor for 20~150 sec through the pneumatic tube. The thermal neutron flux was 2.01×10^{12} $n\cdot cm^{-2}\cdot s^{-1}$ where the Cd ratio was 10±1%. The dose rate for the mixed field radiation was about 45 Gy/sec (4.5×10^3 rad/sec), and the temperature was 45°C.

2·2 Analysis of products

The Co^{II}-EDTA solution containing ^6Li can

induce the following reactions by neutron irradiation:

$$Co^{I}\text{-EDTA} \xrightarrow[(n_f,\gamma)]{(\alpha,{}^3H)} Co^{2+} + \text{other radiolytic products}$$

The variation of the optical density of the Co^{I}-EDTA solution at 540 nm was measured on a Beckman spectrophotometer Model 26. The net variation due to charged particles was determined from the difference of optical densities between irradiated solutions with and without ^6Li added. The radiolytic products were measured with a CAMAC type electrophoresis instrument. The paper strip used was the Whatman chromatograph paper, 2 cm wide and 48 cm long. The buffer solution contains 0.1M CH_3COOH and CH_3COONa and the applied voltage was 1800 V. After 30 min, the paper was placed beneath an infrared light till dryness. The sample paper was cut into several 1 cm sections, and the activity was measured with a NaI(Tl) scintillation counter.

3. Results

3·1 Spectral changes of Co^{I}-EDTA solution by irradiation

Changes of the absorption spectrum of the Co^{I}-EDTA solution in 0.8N H_2SO_4 saturated with air are shown in Fig. 1. The spectra 1a and 1b are for an unirradiated solution and irradiated solution without ^6Li, respectively; the dose of the reactor mixed field radiation was 270kGy (2.7×10^5 rad) The spectra 1c, 1d, and 1e are for the irradiated solutions with ^6Li(0.513%) added; the dose of the charged particles were 23, 46 and 69 kGy (2.3×10^6, 4.6×10^6 and 6.9×10^6 rad), respectively. No change of the shape of the spectra was observed, whether it was due to the reactor mixed field radiation or charged particles. The optical density of the absorption peak decreases as the dose increases. An earlier investigation[5] revealed that the radiolytic products of Co^{I}-EDTA solution with γ-rays are Co^{2+} ion, EDTA, and Co^{I}-EDTA, etc. The absorption peaks of Co^{2+} ion and EDTA are both in the UV region. Although the absorption peak wavelengths of Co^{I}-EDTA and Co^{I}-EDTA are very close to each other, no interference may be expected because of very small amount of Co^{I}-EDTA. The optical density of Co^{I}-EDTA solution with ^6Li added was found not to change appreciably at least 3 days before irradiation and 2 days after irradiation at room temperature. Both the preparation of solution and the determination of absorption change after irradiation were done within one day.

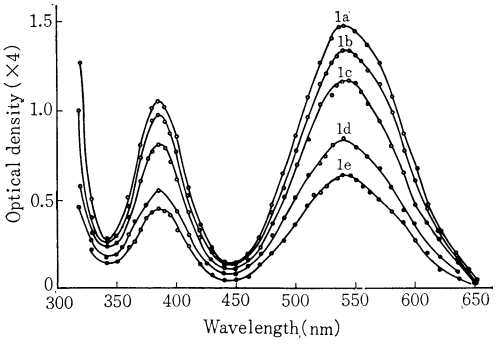


Fig. 1 Change in spectrum of Co^{I}-EDTA solution before and after irradiation.
1a: unirradiated sample, 1b: dose of reactor mixed field radiation=1.75 kGy (1.75×10^5 rad), 1c: dose of charged particles=23 kGy (2.3×10^6 rad), 1d: dose of charged particles =46 kGy(4.6×10^6 rad), 1e: dose of charged particles=69 kGy (6.9×10^6 rad).

3·2 Relationship between absorbed dose rate and G($-Co^{I}$-EDTA)

The effect of absorbed dose rate of charged particles was investigated by changing the amount of ^6Li in the solution. Figure 2 presents the change in G($-Co^{I}$-EDTA) at different absorbed

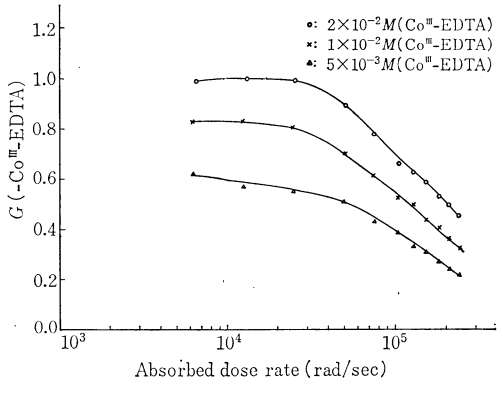


Fig. 2 Relationship between absorbed dose rate and G($-Co^{I}$-EDTA).

dose rates with identical irradiation time. The G(-Co^{I}-EDTA) decreases as the absorbed dose rate increases. In the case of γ radiolysis of Co^{I}-EDTA solution, the G(-Co^{I}-EDTA) is independent of dose rate[5),6)]. The changes in optical density at 540 nm at various dose rates from 62.3 Gy/sec to 2.45 kGy/sec (6.23×10^{3} to 2.45×10^{5} rad/sec) with the same irradiation time are presented in Table 1. With ^{6}Li added, the change of optical density in solution increases as the dose rate increases. Without ^{6}Li added, the optical density remains unchanged for the reactor mixed field radiations. The error of this

Table 1 Change in optical density of solution at various absorbed dose rates

Dose rate (rad/sec)	Optical density(×2) at 540 nm	
	with ^{6}Li	without ^{6}L
2.45×10^{5} (1.54%)	0.648	1.335
2.18×10^{5} (1.368%)	0.674	1.336
1.38×10^{5} (1.197%)	0.760	1.336
1.56×10^{5} (1.026%)	0.796	1.332
1.30×10^{5} (0.855%)	0.853	1.337
1.03×10^{5} (0.684%)	0.862	1.332
7.65×10^{4} (0.513%)	0.952	1.339
5.00×10^{4} (0.342%)	1.054	1.339
2.50×10^{4} (0.171%)	1.163	1.336
1.25×10^{4} (0.085%)	1.218	1.337
6.23×10^{3} (0.043%)	1.276	1.334

Remarks:

1. The parenthesis means percentage of ^{6}Li added.
2. The concentration of solution is $1\times10^{-2}M$. (10^{3} rad=10 Gy)

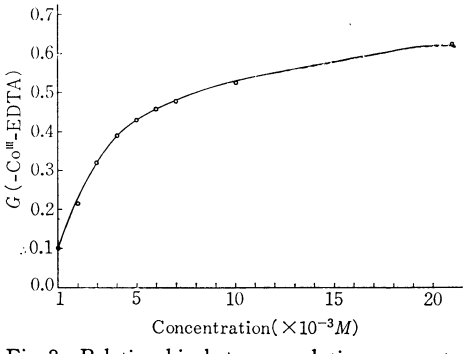


Fig. 3 Relationship between solution concentration and G(-Co^{I}-EDTA). Absorbed dose rate: 1.03 kGy (1.03×10^{5}rad)/sec.

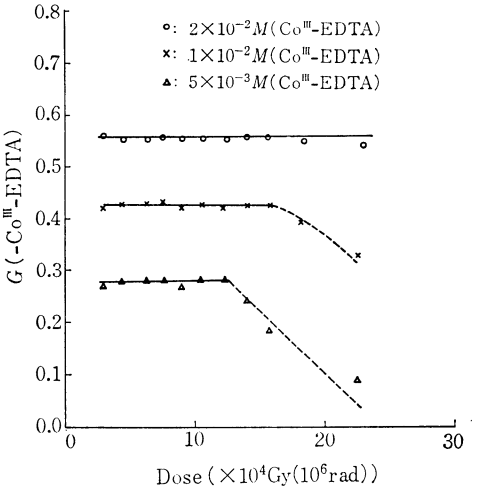


Fig. 4 Relationship between absorbed dose and G(-Co^{I}-EDTA) at the same dose rate. Absorbed dose rate: 1.56 kGy (1.56×10^{5} rad)/sec.

experiment is within 3~6%. Figure 2 indicates that the G(-Co^{I}-EDTA) is dependent on the concentration of Co^{I}-EDTA. Figure 3 shows that the G(-Co^{I}-EDTA) increases steeply in the low concentration range of Co^{I}-EDTA and then tends to level off at an absorbed dose rate of 1.03 kGy/sec (1.03×10^{5} rad/sec) with 60-sec irradiation.

3·3 Relationship between dose and G(-Co^{I}-EDTA) under the constant absorbed dose rates

The dose effect on G(-Co^{I}-EDTA) at an constant absorbed dose rate with different irradiation time is shown in Fig. 4. These results show that, within proper irradiation time, the G(-Co^{I}-EDTA) does not change under different absorbed doses. Nearly constant G-values are obtained when the extent of radiolysis of solution does not exceed 80%: for the solutions of $2\times10^{-2}M$, $1\times10^{-2}M$, and $5\times10^{-3}M$, doses should be less than 230, 150, and 125 kGy (2.3×10^{7}, 1.5×10^{7}, and 1.25×10^{7} rad), respectively.

3·4 The effect of solution temperature on the G(-Co^{I}-EDTA)

The temperature at the pneumatic tube of the 1 MW Tsing Hua Open-pool reactor was about 45°C. The increase in temperature was found

to be 0.4°C for $2\times10^{-2}M$ solution without ^{6}Li irradiated for 120 sec. Under similar conditions, the increase in temperature was 3.5°C and 7°C for solution with ^{6}Li (1.197%) irradiated for 60 and 120 sec, respectively. Table 2 shows the

Table 2 The effect of solution temperature on the G(-Co^{I}-EDTA)

concentration / G(-Co^{I}-EDTA) / Temperature	$2\times10^{-2}M$	$1\times10^{-2}M$	$5\times10^{-3}M$
12°C	0.52	0.41	0.28
25°C	0.60	0.44	0.32
60°C	0.61	0.46	0.32

Remarks:
1. Absorbed dose rate=1.30 kGy(1.30×10^{5}rad)/sec
2. Irradiation time=60 sec

effects of solution temperature on the G(-Co^{I}-EDTA). It is apparent that the effect of the solution temperature on the G(-Co^{I}-EDTA) is negligibly small between 25 and 60°C. The present experiment was carried out at room temperature, and the increase in temperature in the solution containing ^{6}Li has negligible effect on the G(-Co^{I}-EDTA).

3·5 Determination of radiolytic products in Co^{I}-EDTA solution

In order to increase the sensitivity of measurement, the determination of radiolytic products was performed by using ^{60}Co labeled Co^{I}-EDTA. The results of the paper electrophoretic analysis of the irradiated solution is shown in Fig. 5. Figure 5a and 5b show the results for the solution without ^{6}Li irradiated with the reactor mixed field radiation and with 1.197% ^{6}Li irradiated with charged particles to 110 kGy (1.10×10^{7} rad). Whether the solution contains ^{6}Li or not, the resulting charts obtained are similar, and the similar result was obtained with γ-irradiation[6),7)]. The peaks at "a" near the cathode and at "b" and "c" near the anode were determined to be due to Co^{2+} ion, Co^{I}-EDTA, and Co^{I}-EDTA, respectively.

4. Discussion

The radiolysis of Co^{I}-EDTA solution with

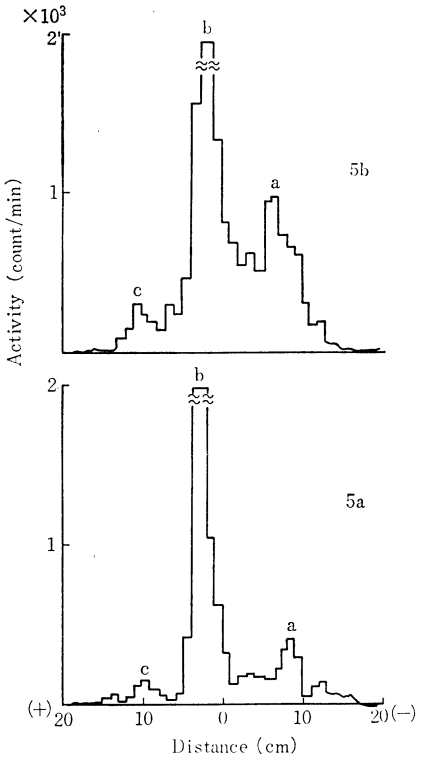


Fig. 5 Results of electrophoretic analysis of radiolytic products.
5a: dose of reactor mixed field radiation=2.75 kGy (2.75×10^{5} rad), 5b: dose of charged particles=110 kGy (1.10×10^{7} rad).

charged particles through the ^{6}Li(n,α)^{3}H reaction seems similar to that with ^{60}Co γ-rays as far as the change in spectrum, effects of concentration, temperature, and radiolytic products are concerned. However, the relationship between the dose rate and the G(-Co^{I}-EDTA) was found to be different. These differences may be due to the fact that the range of charge particles in solutions is much shorter than that of γ-rays and the different spatial distribution of initial products. The energy is absorbed by a thin layer of molecules around Li^{+} ions only; and the produced H, OH, HO_2, and H_2O_2 will cause the decomposition of Co^{I}-EDTA within a few layers of the solution. Due to the recombination effect, the decomposition yield of Co^{I}-EDTA is thus regarded as insensitive to the increasing dose rates. Therefore the G(-Co^{I}-EDTA) de-

creases as the absorbed dose rate increases. The mechanism of radiolysis of Co^{II}-EDTA solution with charged particles is a subject for further investigations.

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要　旨

$^6Li(n, \alpha)^3H$ 反応で生じた荷電粒子による Co^{II}-EDTA 溶液の放射線分解

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$^6Li(n, \alpha)^3H$ 反応で生じた荷電粒子による Co^{II}-EDTA の0.8N 硫酸溶液（空気飽和）の放射線分解を分光測光法により研究した。

実験の結果，吸収線量率の増加にしたがい，$G(-Co^{II}\text{-EDTA})$ 値は減少することがわかった。また，同じ吸収線量率では，吸収線量を変化させても，$G(-Co^{II}\text{-EDTA})$ 値は変わらなかった。試料濃度，温度の影響についても検討を行った。