Plausible Applicability of Aqueous Congo Red Dye System as Secondary Gamma-ray Dosimeter

I. DAS SARMA* and D. V. PARWATE

Department of Chemistry,
Rashtrasant Tukadoji Maharaj Nagpur University, Nagpur – 440 033, India.

*dassarmaindrani@rediffmail.com

Received 18 November 2007; Accepted 10 January 2008

Abstract: Aqueous congo red dye solutions in the concentration range of 0.01–0.03mM were irradiated for varying γ doses 0.050 kGy to 0.150 kGy. The molar extinction coefficient of the dye solution of congo red was found to be 2.70×10^5 at its absorption maxima 499.0 nm. No change in λ_{max} was observed on irradiation. As the dye solutions are sensitive towards γ -irradiation, decolouration occurs on irradiation. The G-values for the doses in between the range of 0.035 kGy to 0.125 kGy were found to be practically constant for pure aqueous systems. Hence this was used to determine the dose of the gamma source. With the addition of alcohols in the systems, degradation of the dyes due to radiations decreased considerably.

Keywords: Congo red, G-value, Radiolytic decomposition, Alcohols

Introduction

A system that measures the amount of energy absorbed from the ionizing radiation by virtue of the chemical changes produced in the system on exposure to the radiations is a chemical dosimeter¹. The high energy radiations bring about the radiolysis of the dyes (decolouration or bleaching effect) which is used as a measure of the energy of the radiation incident on the system. The use of solutions of dyes such as methylene blue², chlorantine fast green BLL³ and coumarine⁴ for chemical dosimetry is reported. Congo red (C. I. No. 22120) or the di sodium salt of diphenyl diazo *bis*-1-naphthylaminesulphonic acid is brownish red powder having absorbance maxima at 499.0nm in aqueous medium. The aqueous solution has pH 7.3 and the systems were stable for several hours. The decolouration of the dye as a result of γ -irradiation may be delayed using certain additives. In the present paper we have investigated the effect of alcohols in delaying the degradation of the dye. An attempt is made to explore the possible use of the aqueous congo red systems as high energy dosimeter. Ajji⁵ reported that alkaline methyl red dye solution could be used as chemical dosimeter for gamma rays in the range between 50 and 6000Gy.

Experimental

Three concentrations of congo red dye solutions (0.01, 0.02 and 0.03 mM) were studied with various concentrations of methanol (0.31, 0.62 and 1.24 M), ethanol (0.21, 0.42 and 0.86 M) and 1-propanol (0.17, 0.33 and 0.67 M). All the solutions were prepared fresh using doubly distilled water and the pH of the systems were found to be 7.3. The absorbances of the irradiated solutions were recorded within ten minutes of irradiation, even though the stability of the solutions was quite higher (120 hours for unirradiated and 1.5 hours for irradiated solutions). Gamma irradiation was carried out in stoppered corning glass tubes having B24 standard joints in Cobalt-60 Gamma Chamber (GC 900) at a dose rate of 0.92 kGy h^{-1} ($5.741 \times 10^{18} \text{ eV g}^{-1} \text{ h}^{-1}$). The dose rate was verified by Fricke dosimetry. Absorbed dose correction was carried out for calculation purpose using Z/A values for the system and Fricke dosimeter. The amount of dye decomposed was estimated by recording the absorbance at 499.0nm on Shimadzu UV 240 spectrophotometer.

Results and Discussion

Pure aqueous congo red dye solution in the concentration range of 0.01–0.03mM were irradiated for varying γ doses of 0.050–0.150 kGy. The decolouration due to irradiation with gamma rays showed a linear function up to 0.150 kGy with respect to the absorbed dose in aqueous systems as can be seen in Figure 1.

Figure 1. The graphs depicting radiolytic degradation of pure aqueous congo red dye solutions of 0.01, 0.02 and 0.03 mM.

It was expected that λ_{max} would get altered on γ -irradiation. However neither there was a change in λ_{max} (499.0nm) for the aqueous solution of the dye on γ -irradiation nor was it observed for aqueous solutions containing varying amounts of different alcohols. Our previous work⁶ suggests that G-values for the congo red dye decomposed for doses in the range of 0.035 kGy to 0.125 kGy to be practically constant 57.69–68.26 molecules (per 100eV) for concentration range of 0.01–0.03 mM in pure aqueous systems.

The dose required to bring the concentration of dye for 0.01 mM system to 0.0071 mM was found to increase from 0.050 kGy in pure aqueous systems to 1000Gy in aqueous alcoholic systems. Further from the graph as shown in Figure 2, it can be concluded that there is practically no decomposition of dye up to 0.750 kGy of dose absorbed. Beyond this limit degradation is linear up to 1.750 kGy. The discoloration of the dye made it impossible to study the radiolytic degradation beyond 2.000 kGy.

It is inferred from Figure 3 that the detection limit of gamma dose, 1.750 kGy is not affected by increasing the concentration of the alcohols up to 5% (or 1.24, 0.86 and 0.64 M for methanol, ethanol and 1-propanol respectively).

Figure 2. Radiolytic degradation of 0.01, 0.02 and 0.03 mM congo red dye solutions in 5% aqueous methanol.

Figure 3. The graphs depicting radiolytic degradation of 0.03 mM congo red dye solutions containing 1.25%, 2.5% and 5% methanol.

The Figure 4 depicts the trend for $G(-\text{dye})$ with dose rate. The graph initially declines upto 0.750 kGy with increase in dose and thereafter it becomes more or less steady. This may be attributed to the presence of alcohols in the systems which retard degradation by interacting with the radicals that are generated in the systems. After a certain dose limit (0.750 kGy) all the alcohols get used up there by accelerating the degradation of the dye with dose absorbed.

On γ -irradiation, aqueous systems are known to produce e_{aq}^- , $\text{H}^\bullet$ and $\text{OH}^\bullet$ as primary radicals. Also alcohols are well-known as $\text{H}^\bullet$ and $\text{OH}^\bullet$ radical scavengers. Methanol⁷ reacts with $\text{H}^\bullet$ and $\text{OH}^\bullet$ radicals either by abstracting a hydrogen atom from carbon or oxygen atom as shown in expressions (i) and (ii).

Since the rate constant is the same for abstraction of hydrogen attached either to carbon or oxygen atom in methanol molecule, both the reactions are equally possible.

Figure 4. Trend for G-values in the accordance with the dose exposed in 5% methanol system.

In air saturated systems interaction of e_{aq}^- at higher pH (7.3 in present systems) is low as they are readily scavenged by the dissolved O_2 . Nevertheless, probability of interaction of e_{aq}^- with the water and alcohol in the system cannot be ignored. The reaction of e_{aq}^- with water or alcohol in the systems is quite slow as is evident from the rate constants given in (iii) and (iv) respectively.

At lower concentrations of methanol ($< 10^{-2}\text{M}$) reaction of e_{aq}^- with water (iii) predominates rather than that with methanol (iv). This reaction (iv) is very slow and competes with (iii) and other reactions of e_{aq}^- only at high concentrations of methanol (above 10^{-2}M). Since the concentration of the methanol (0.31, 0.62 and 1.24 M respectively) in the systems studied are high enough, it is likely that the reaction with e_{aq}^- proceeds via reaction (iv) instead of (iii).

According to Spinks and Woods⁷ the radiolytic degradation of ethanol and 1-propanol are quite similar to that of methanol where $\text{H}^\bullet$ and $\text{OH}^\bullet$ radicals react with the alcohol by abstracting H mainly from α carbon atom whilst the e_{aq}^- in virtue of its less reactivity possesses lesser chances of the dye degradation. The radicals formed by H abstraction rapidly add oxygen, forming peroxy radicals in air saturated solutions which subsequently form hydrogen peroxide and carbonyl compounds.

Thus the protection brought about by the addition of the alcohols can be attributed to the fact that the latter being scavengers react with the $H^\bullet$ and $OH^\bullet$ radicals generated due to the radiolysis of the water thereby reducing the chances of interaction of the dye molecule with the radicals. The data shows that alcoholic aqueous systems containing congo red dye can be proposed as a secondary gamma ray dosimeter in the probable dose range of 500–1750 Gy. Further studies using different γ sources of various energies and dose rates are requisite to optimize the exact operating dose range of the dosimeter.

Acknowledgements

The authors thank the Head, Department of Chemistry, Rashtrasant Tukadoji Maharaj Nagpur University for providing the irradiation and laboratory facilities for the current work.

References

1. Gupta B L and Bhat R M, Handbook on calibration of high-dose radiation facilities (BARC), 1983, Chapter 1.
2. Vereshchinski I V and Pikaev A K, Introduction to Radiation Chemistry, Ed. Prof. G. Stein, Israel Program for Scientific Translations, Jerusalem, 1964, 272.
3. El-Assy N B, El-Wakeel E S and Abdel Fattah A, *Int J Rad Appl Instrum [A]*. 1991, **42**, 89.
4. Collins A K, Makrigiorgos G M and Svensson G K, *Med Phys*. 1994, **21**, 1741.
5. Ajji Z, *Radiation Measurements*. 2006, **41**, 438.
6. Parwate D V, Das Sarma I and Batra R J, *Radiation Measurements*. 2007, **42**, 1527.
7. Spinks J W T and Woods R J, An Introduction to Radiation Chemistry, 2nd Ed., Wiley Interscience Publications, New York, 1975, 317.