Applied Radiation and Isotopes 74 (2013) 152–156

Contents lists available at SciVerse ScienceDirect

Applied Radiation and Isotopes

journal homepage: www.elsevier.com/locate/apradiso

Tracing of γ-radiation-induced electrical conductivity and pH change of hexamethylenetetramine aqueous solutions and its applications

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HIGHLIGHTS

- γ-Radiation induces electrical conductivity and pH change of HMTA solutions.
- Factors affecting γ-radiation induced electrical conductivity and pH change of HMTA solutions were studied.
- HMTA aqueous solution could be considered as a dosimiter for radiation.

ARTICLE INFO

Article history:
Received 6 January 2012
Received in revised form
1 December 2012
Accepted 8 December 2012
Available online 20 December 2012

Keywords:
Chemical dosimeter
γ-radiation
Hexamethylenetetramine
Electrical conductivity
pH

ABSTRACT

The interest in studying γ-radiation effects on hexamethylenetetramine (HMTA) is due to its importance in nuclear fuel technology. The current study indicates that γ-radiation induces electrical conductivity (RIC) and pH changes in HMTA aqueous solutions. The effects of HMTA concentration, absorbed radiation dose, absorbed dose rate and storage time on RIC and pH changes were studied. HMTA aqueous solutions could be considered as a promising γ-radiation dosimeter, in both technical and medical fields.

1. Introduction

In nuclear fuel technology, HMTA plays an important role in the sol–gel method for the preparation of micro spheres of thorium, uranium and plutonium oxides (Lioyd et al., 1976; Homan et al., 1977; IAEA, 2009). In spite of the importance of HMTA in this field, few papers had been published on the effect of γ-radiation on this compound (Dondi et al., 2011).

Cottin et al., 2002 presented their results, on the photodegradation, of HMTA at 122 and 147 nm, which included the formation of HCN, NH_3 and other N bearing molecules. The γ-radiolysis products of aqueous HMTA solutions were identified by Dondi et al., 2011. These products are mainly HMTA methyl-and hydroxy-derivatives. The purpose of the present work is to study the physico-chemical changes of the irradiated aqueous HMTA solutions from the dosimetric point of view. Therefore, the effects of HMTA concentration, absorbed dose, absorbed dose rate, and post irradiation storage time, on the RIC and pH changes, were studied. However, RIC measurement is just one of several physical methods applied to determine absorbed dose (Sife–Eldeen, 2008a, 2008b; Sadovnichii et al., 2003; Sevila et al.,2003; Kesternich et al.,1995; El-Hussieny et al.,1985).

2. Experimental

2.1. Preparation of HMTA aqueous solutions and irradiation

HMTA (Fig. 1) is prepared by the reaction of ammonia and formaldehyde in an aqueous medium according to Eq. (1) (Nekrasov, 1978).

$$4NH_3 + 6HCHO \rightarrow \underset{\mathbf{HMTA}}{(CH_2)_6N_4} + 6H_2O \quad \Delta H = -55\ \mathrm{kcal/mol} \tag{1}$$

HMTA solutions were prepared by dissolving pure calculated amounts of HMTA in double-distilled water, according to the required concentrations. Samples of HMTA solutions (naturally aerated) were γ-irradiated, isotropically at electronic equilibrium condition, by a 4.37 kCi ^{60}Co source (India Gamma chamber 4000 A,). Radiolysis was carried out in 50 ml bottles with tight glass stoppers, at ambient temperature (30 °C). Fricke solution was

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0969-8043/$ - see front matter
http://dx.doi.org/10.1016/j.apradiso.2012.12.004

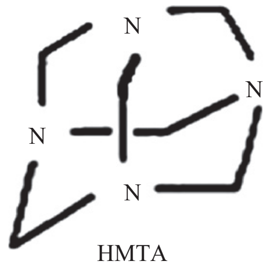


Fig. 1. Hexamethylenetetramine (HMTA).

used as a reference dosimeter to determine absorbed dose rates of the radiation facility, according to ASTM E1026–04e1 Standard Practice. The absorbed radiation dose correction was applied for the difference in the electron densities of HMTA and Fricke solutions. The current study was carried out at different dose rates (0.33–3.38 kGy/h). The dose rate was changed using lead attenuators (50,75 and 90% attenuation).

2.2. Electrical conductivity measurements

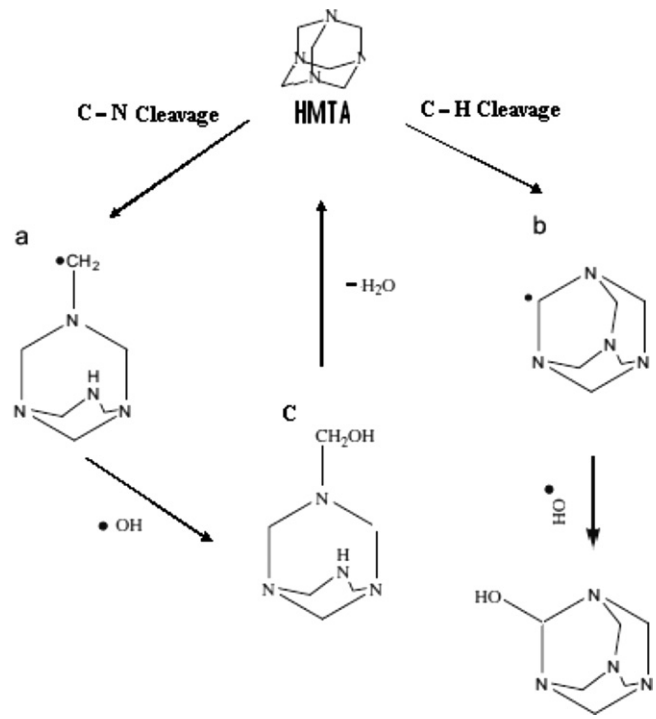
The electrical conductivity was measured at room temperature using the Kent EIL5007 conductivity meter (Kent industrial measurements—Brown Boveri). The conductivity meter was calibrated using KCl standard solutions (CDPR-EHAP, 1999). The electrical conductivity of the irradiated solutions was measured immediately after irradiation and after storage. The irradiated samples were stored under freezing conditions. Each value, in the presented results, is the average of 3 measurements. The relative standard deviation (%RSD), calculated for each set of measurements (n=3), was found to be $\leq 6.1\times10^{-2}$% for all obtained data.

2.3. pH measurements

Measurements of the pH were performed using an Orion Research model SA210 pH/meter. The measurements were carried out at room temperature. Each value, in the presented results is the average of 3 measurements.

3. Results and discussion

HMTA solutions were γ-irradiated by the previously described conditions. Consequently, the electrical conductivity as well as the pH was observed to increase. These observed physical changes could be attributed to the radiation induced formation of products with ionic or polar nature. As HMTA is an amine, it could be supposed that it undergoes typical amine radiolysis. Dondi et al., 2011 found that the main γ-radiation induced decomposition products of aqueous HMTA solutions are its methyl- and hydroxy-derivatives. They concluded that HMTA can undergo a C–N cleavage, thus giving radical (a) or a C–H cleavage producing radical (b) (Scheme 1). Radical (a) may react with OH forming compound (c). Consecutive C–N radiation induced cleavages could lead to a complete degradation of HMTA, giving lower molecular weight compounds. These latter compounds could undergo subsequent radiolysis forming methyl and formyl radicals that, by coupling with (b), can give the observed methyl and formyl-HMTA. Similarly, hydroxy-HMTA is formed by coupling of (b) with hydroxyl radicals coming from the radiolysis of water. HMTA could be formed again, if compound (c) loses H_2O (Dondi et al., 2011). On the other hand, from the photodegradation point of view, Cottin et al., 2002 concluded that photolysis of HMTA with water vapor leads to an efficient degradation with the formation of HCN, NH_3 and other



Scheme 1. Decomposition products of γ-irradiated aqueous HMTA solutions.

N bearing molecules. It is worthwhile to mention that, the degradation process is activated by the photolysis products of water.

Therefore, the observed γ-radiation induced changes, in the electrical conductivity and pH, could be attributed to the formation of polar compounds such as hydroxy-HMTA and formyl-HMTA. On the other hand, according to HMTA photodegradation results (Cottin et al., 2002) the formation of HCN, NH_3 and other N bearing molecules could be related to the observed RIC and pH changes.

In the present work, the following factors were studied: HMTA concentration, absorbed radiation dose, absorbed dose rate, and post irradiation storage time, on the γ-radiation induced changes in the electrical conductivity and pH of HMTA solutions.

3.1. Effect of HMTA concentration

Generally, in the irradiated dilute aqueous solutions ($<$ 0.1 M) all of the energy absorbed is deposited in the water molecules. Hence, the observed chemical changes are the result of the reactions between the solute and the water radiolysis products. On increasing the solute concentrations, the direct radiolysis of the solute gradually becomes important and the solute may also interfere with the spur reactions. Moreover, the solute reacts selectively with the radical products at high concentrations (Choppin et al., 2002).

In order to study the dependence of RIC and pH change on HMTA concentration, different HMTA concentration samples (0.0, 0.02, 0.1, 0.5, 1.0 M) were γ-irradiated at different absorbed doses, 18.15 kGy and 90.53 kGy. It is apparent from (Fig. 2) that the RIC, generally, increases as HMTA concentration increases at different doses. The RIC dependence on HMTA concentration deviates from linearity, as the absorbed radiation dose increases. Moreover, at the same concentration the RIC increases, significantly, as the absorbed radiation dose increases for all studied concentrations. Fig. 3 shows the dependence of the radiation induced electrical conductivity change, $\triangle$EC, on HMTA concentration at different doses (18.15 and, 90.53 kGy), provided that

$$\Delta EC = RIC - EC_{(0)} \quad (2)$$