Radiation Effects on Some Cyanine Dyes in its Aqueous Solvents

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Received: 20/8/2012 Accepted: 15/9/2012

ABSTRACT

The radiation chemical discoloration of aqueous solutions of cyanine dyes were studied using the radiolysis technique. The spectral characteristics of radical were determined and the radiation – chemical yields of their formation and dye decomposition were measured. The degradation of the two types of cyanine dyes with gamma source were studied. Different parameters that effects on the radiolysis such as exposure doses and pH were studied. The UV detector was used to analyze the degradation percentage. The variation of the irradiation doses from 1 kGy to 10 kGy change the degradation from about 55% to 90% with a little difference in the stability of cyanine dyes that contain nitro group (P-NO₂) than dimethyl group P-N(Me)₂ due to the electron with drawing effect of nitro group. The results obtained were used to study the applicability range and sensitivity of different type of cyanine dyes in aqueous solution to be used in chemical dosimetry purposes.

Key words: Water; Cyanine ; Dyes; Gamma

INTRODUCTION

Cyanine dyes have been used for a long time as photo sensibilizer, passive shutters and active media of lasers, fluorescent probes photo resistors and new media for information recording (¹). It was also suggested that these compounds can be used markers for biological molecules (², ³). Biological activity of cyanine has been also reported recently (⁴).

The ability of cyanine dyes to form complexes with metals results in significant expansion of application area for these molecules. In solid state, the complexes of cyanine dyes are potential objects for physics of semiconductors and nonlinear optics. In solutions and colloid systems, they can be used as unique markers of biological molecules.

Complex formation may also favor the transformation of biologically active compounds of cyanine series into water-soluble forms (⁵) in addition; the same complexes of cyanine dyes may be used in analytical chemistry (⁶) and in solution of ecological problems.

Methine Cyanine dyes have attracted much attention because of their potential application in organic functional materials (⁷,⁸). In recent years; they have been used extensively as optical recording materials (⁹). Cyanine dyes with short methane chains are readily soluble in common organic solvents such as ethanol and acetone. However, a convenient method for synthesis of these short methine chains still needs to be developed.
The majority of methine cyanines reported for use in optical recording materials belong to the class of symmetrical cyanine dyes, whereas unsymmetrical methine cyanines have superior optical properties and alcohol solubility.

A prominent, narrow and strongly red shifted band has been signature for aggregate formation by numerous cyanines since their discovery by jelly (10) and scheibe (11). Despite extensive investigation, the spectral changes following self-aggregation and the kinetics of aggregate formation in solution/thin films are still debated.

The present work aimed to study the radiation degradation / decoloration for two-type of cyanine dyes in aqueous solutions under the effect of gamma irradiation in order to use it as chemical dosimeters. On the other hand, using the radiolysis technique may used to remove the color from industrial waste.

EXPERIMENTAL AND METHODS

Preparation:
Dye solutions were prepared by using compounds 4-Benzylidene-2-methyloxazol-5-one derivatives (1a-e) as starting material, which prepare according to Vogel’s textbook of practical organic chemistry (12).

\[
\begin{align*}
(1a-e): & \ A = \text{H (a)}; \ A = \text{P-OCH}_3 \ (b); \ A = \text{P-NO}_2 \ (c); \ A = \text{P-OH} \ (d); \ A = \text{P-N(Me)}_2 \ (e).
\end{align*}
\]

- Synthesis of compounds 4-Benzylidene-3-ethyl iodide-2-methyloxazol-5-one derivatives (2a-e):-
  By adding, an amount of compound 4-Benzylidene-2-methyloxazol-5-one derivatives (1a-e) in a flask then witted it by ethyl iodide solution, heating the mixture gently in water bath for about 30 minutes, reflux the mixture for about 1 hour using ethanol as solvent. The reaction mixture was filtrated from unreacted materials. The filtrate was concentrated and cooled. The precipitated products separated, filtrated and crystallized from ether, Equation (1).

\[
\begin{align*}
\text{Substituents of equation (1): } & \ A = \text{H (a)}; \ A = \text{P-OCH}_3 \ (b); \ A = \text{P-NO}_2 \ (c); \ A = \text{P-OH} \ (d); \ A = \text{P-N(Me)}_2 \ (c).
\end{align*}
\]
Synthesis of dyes 4-Benzylidene-3-ethyl iodide-5-one mono-2[4] methine cyanine dyes derivatives (3a, b):

An ethanolic solution of equimolar of (2c, e) and quinoline ethiodide salts in the presence of few drops of piperidine were refluxed for 1 hour on a hot plate. The reaction mixture were filtrated from unreacted materials. The filtrate concentrated to one third of its volume, cooled and acidified with acetic acid. The precipitated products after dilution with water were separated, filtrated and crystallized Equation (2).

\[ \text{Equation (2)} \]

Substituent’s of equation (2):

(2c, e): A = P-NO\(_2\) (c); A = P-N(Me)\(_2\) (e).

(3a, b): A = P-NO\(_2\) (a); A = P-N(Me)\(_2\) (b).

The solution in various pH about 2, 5, 7, 9 and 12 were prepared from two type of the cyanine dyes under this investigation P-NO\(_2\) and P-N(Me)\(_2\) that used in this work.

Irradiation and measurement:

Gamma irradiation source in the National Center for Radiation Research and Technology, Atomic Energy Authority, Cairo, Egypt was used (Indian Co-60 gamma cell type GE-4000 A with activity about 5511.1 Ci in 23 June 2010). The exact irradiation dose used was determined daily for the irradiation system based on Co-60 decay. All irradiation were carried out at ambient temperature for the doses (1,5,10 kGy) at different pHs which adjusted by NaOH / HCl. Measurement of the optical absorbance was carried out immediately after irradiation. The degradation products were determined using UV detector. The degree of degradation of the dye was calculated from the decrease of maximum absorbance by using the following equation (13):

\[ \text{Degradation} \% = \frac{A_0-A_i}{A_0} \times 100 \quad \ldots \ldots \ldots \ldots (3) \]

Where: \(A_0\) and \(A_i\) are the absorbance’s before and after irradiation, respectively.

RESULTS AND DISCUSSION

The structure of cyanine dyes with different function groups (equation 2). The decline of pH upon irradiation indicated that formation of acidic product, and the identified products were compared with standard used for the preparation of dyes. The formation of acetic anhydrous that could be detected as degradation products of the dyes were shown in figures 1,2,3. The degradation percentage calculation from equation (3) as a function on pHs at different exposure doses. It was found that with increasing the exposure dose the degradation percent is increasing from about 55% to 90 % for both P-NO\(_2\) and P-N(Me)\(_2\) cyanine dyes.
In comparison between dyes (3a) P-NO\textsubscript{2} and (3b) P-N(Me)\textsubscript{2} (equation 2), it was found that the weakly degradation of P-NO\textsubscript{2} than P-N(Me)\textsubscript{2} cyanine dyes. This may be due to the electron withdrawing effect (Negative Inductive effect) of nitro group, which increase the stability of this dye. On the other hand, dye (3b) degrade strongly, this may be due to the electron donating group (positive Inductive effect) of N(Me)\textsubscript{2} group which decrease the stability of this dye.\textsuperscript{(14,15,16)}

The degradation at different pH values for the dyes under this investigation were studied by irradiating aqueous using exposure doses 1, 5 and 10 kGy. The dependence of the degradation process on pH shown in Figs. 1, 2 and 3. The degradation percent is decreasing with increase the pH value at different exposure doses. Observation behavior of the effect of the pH on the degree of degradation is not quite clear. However, possible explanation might be depend on the acid-base properties of the OH radicals. In strong basic solution, the OH radicals dissociate to the less reactive O\textsuperscript{-} radicals:

\[
\text{OH} \rightleftharpoons H^+ + O^- 
\]

In fact, the degradation depends on the relative reactivity of the various species, availability of oxygen, dose and pH of the solution (acidic solution)\textsuperscript{(17)}:

\[
e^{-}_{\text{aq}} + H^+ \rightarrow H^-. 
\]

The reducing H atoms are scavenged by oxygen leading to a formation of HO\textsuperscript{2-}which can be involved in the degradation process. The O\textsuperscript{2-} species are not very reactive but at pH>7 the ‘OH radicals are the major primary attacking transients. The sharp decrease in the degradation at pH>9 may be a result of the low reactivity of O\textsuperscript{-} and O\textsuperscript{2-} species to the attack of the dyes and this agree with other investigators N. Ggetoff, (1997)\textsuperscript{(17)} and I. Bas Sarma et al., (2008)\textsuperscript{(18)}.

![Fig. (1) Effect of pH on the degradation of cyanine dyes at 1 kGy](image-url)
CONCLUSION

Fig. (2) Effect of pH on the degradation of cyanine dyes at 5 kGy

Fig. (3) Effect of pH on the degradation of cyanine dyes at 10 kGy
We can concluded that the cyanine dyes in aqueous solvent could possibly applied as chemical dosimeters under certain conditions. The relationship found between absorbance and concentration verified by using beers law, which confirmed that cyanine dyes might be used as a dosimeter over a high range of gamma dose ranging from 1 to 10 kGy. In addition the stability of P-NO₂ is higher than P-N(Me)₂ cyanine dyes due to the electron with drawing effect of nitro group and the electron donating group (positive inductive effect) of N(Me)₂ group that leading to decrease the stability of the dye. However, additional studies are still required to increase the sensitivity of cyanine dyes to cover a wide range of exposure doses.

ACKNOWLEDGEMENTS

Many thanks to Dr. Islam. M. Abdellah, Department of Chemistry, Faculty of Science, South Valley University for contributing in the idea and the chemical synthesis of dyes during the work.

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