### FLUORESCENCE AND GAMMA RADIATION STUDIES ON SOME DYES AND ITS ANALYTICAL IMPLICATIONS

THESIS SUBMITTED
BY

Wafaa Badr El-Din Moustafa

(M.Sc. in Chemistry)
National Centre for Radiation Research and Technology

47.86

FOR

Ph.D. Degree

(Chemistry)

50125

TO

Faculty of Science Ain Shams University

Cairo, Egypt.

1994



## Dedicated to My husband

Dr. Gehad M. Allia



#### ACKNOWLEDGEMENT

The author wishes to express her deep appreciation to Dr. Mohamed Sabry Ahmed Abdel-Mottaleb, professor of chemistry, Faculty of Science, Ain Shams University, for suggesting the point of research, supervision, his patience, leadership, and following the progress of the work with keen interest, valuable advice and guidance.

Deep thanks have to go to Dr. F. Abdel-Rehim, professor of Radiation chemistry, National Center for Radiation Research and Technology for suggesting the problem, supervision, guidance, motivation, time, and continuous help during all the stages of the development of the work.

I would like to thank **Dr. M. Antonious**, associate professor of chemistry, Faculty of Science, Ain Shams University for help and guidance.

The author expresses also her thanks to Dr. Y. El-Sayed for providing some of the compounds studied.

The author is grateful to professor Dr. Ahmed El. Miligy, chairman of National Center for Radiation Research and Technology (NCRRT), Atomic Energy Establishment, for his continuous encouragement and support.

Finally, deep appreciation is extended to all members of Radiation Dosimetry Department, NCRRT specially Dr. A. Abdel Fattah for their co-operation and also all the persons of NCRRT for their help and assistance.

# FLUORESCENCE AND GAMMA RADIATION STUDIES ON SOME DYES AND ITS ANALYTICAL IMPLICATIONS.

Thesis Advisor

Approved

Prof. Dr. M.S.A. Abd-El-Mottaleb

Prof. Dr. F.M.M.Abd-El-Rehiem

Dr. M.S. Antonious

2 Pal

مامرسم

Head of Chemistry Department

Prof. Dr. A.F.M. Fahmy

A-F.M-Fahmy

Name of Student: Wafaa Badr El-Din Moustafa

Degree Awarded: B.Sc. in Chemistry-Geology, 1982.

M.Sc. in Chemistry , 1987.

Faculty : Science

University : Ain Shams.

### CONTENTS

	Page
AIM OF THE WORK	i
CHAPTER I: INTRODUCTION	
∮1.1. Effect of Solvent.	1
∮1.1.1 Single-Parameter Approach.	4
∮1.1.2 Multi-Parameter Approach.	4
∮1.2 Fluorescence Spectroscopy.	12
₹1.2.1 Fluorescence, Phosphorescence and	
Emission Quenching.	12
∮1.2.2 Kinetics of Quenching: Stern-Volmer	
Equation.	17
<b>∮</b> 1.3 Quenching Mechanisms.	21
∮1.3.1 Excimer Formation.	21
<pre>\$1.3.2 Exciplex Formation.</pre>	22
∮1.3.3 Charge-Transfer (CT) Absorption	
Transition.	24
\$1.3.4 Electronic Energy Transfer Mechanisms.	29
₹1.4 Effect of Viscosity and Temperature.	30
₹1.4.1 Quantum Yields.	30
∮1.4.2 Determination of Quantum Yields.	32
∮1.5 Dosimetry for Radiation Processing.	36

		Page
<b>∮</b> 1.6	Interaction of Gamma Radiation with Matter.	40
∮1.7	Radiation Quantities.	40
	∮1.7.1 Absorbed Dose and Dose Rate.	40
	£1.7.2 Exposure and Exposure Rate.	43
	<b>§</b> 1.7.3 Radiation Chemical Yields.	44
<b>∮</b> 1.8	Importance of Dosimetry in Radiation	
	Processing.	46
<b>∮</b> 1.9	Literature Survey on Chemical Dosimetry.	47
CHAPTER II:	EXPERIMENTAL	
∮2.1	Preparation.	56
∮2.2	Instrumentation and method.	56
	\$2.2.1 Absorption Spectra.	<b>5</b> 6
	∮2.2.2 Emission Spectra.	56
	\$2.2.3 Fluorescence Quantum Yield	
	Determination.	57
	₹2.2.4 Fluorescence Quenching.	57
	₹2.2.5 Gamma Radiations.	58
<b>∮</b> 2.3	Irradiation Procedure.	59
	₹2.3.1 Preparation of Solution.	59
	\$2.3.2 Calibration of the Radiation Field.	59
	\$2.3.3 Irradiation of Different Solutions.	65
	∮2.3.4 Analysis of the Spectra.	65

	Page
∮2.4 Calculations.	66
\$2.4.1 Calculations of G-Value.	66
CHAPTER III: RESULTS AND DISCUSSION	
A. PHOTOPHYSICAL PROPERTIES OF FLUORESCENT PROBES.	68
§3. A.1. Solvent Effect on Absorption Spectra.	68
∮3.A.2. Solvent Effect on Fluorescence Spectra.	69
B. FLUORESCENCE QUENCHING BY SOLVENTS	72
$$3.B.1$ Quenching of Dye (2) by $K_3[Fe(CN)_6]$	
in 20% EtOH/ $H_2^0$ .	73
$\$3.B.2$ Quenching of Dye (2) by $K_4[Fe(CN)_6].3H_2O$	
in 20% EtOH/H <sub>2</sub> O.	74
\$3.B.3 Quenching of Dye (2) by Iodine	
in Chloroform.	74
\$3.B.4 Quenching of Dye (5) by K <sub>3</sub> [Fe(CN) <sub>6</sub> ]	
in 80% EtOH/ $H_2$ 0.	75
\$3.B.5 Quenching of Dye (5) by Iodine	
in Chloroform.	75
C. EFFECT OF VISCOSITY MEDIUM	101
D. DOSIMETRIC STUDIES BASED ON THE RADIATION INDUCED	
BLEACHING OF DYE 2 AND DYE 6 IN ORGANIC SOLUTION.	125
∮3.D.1. Preliminary Optical Measurements.	126
63 D 2 Radiation Studies	127

	•	Page
5	∮3.D.3 Degradation Kinetics.	128
S	∮3.D.4 Response Curves.	130
5	∮3.D.5 Color Stability.	130
SUMMARY		145
REFERENCES		150
ARABIC SUMM	MARY	

Aim of The Work

### AIM OF THE WORK

Great attention has recently been paid to the problem of solvent effect on spectral, chemical and reactivity data of electron donor-acceptor molecules (EDA) of potential industrial applications. In this thesis some photophysical parameters of EDA dyes (1-4) will be studied in different media.

The study includes measuring the fluorescence quantum yields  $(\Phi_f)$  as a function of viscosity of the medium (in glycerol at different temperatures).

Since quenching processes of radiant energy have significant bearing on structure requirements necessary to get essential information about some photochemical steps in a variety of solar energy conversion systems for increasing the efficiency of producing active quenchers, and because they provide molecular level information about excited state energy transfer which is routinely used in lasers and in molecular yardstick, the thesis will deal with these processes.

In particular, the absorption and fluorescence spectra of two dyes (2 and 5) will be measured precisely upon the addition of several inorganic fluorescence quenchers. We will report on the factors affecting the rate constant of fluorescence quenching of the above dyes by heavy atom induced by using iodine as quencher

and by electron transfer due to excited state interactions with some inorganic complexes like  $K_3[Fe(CN)_6]$  and  $K_4[Fe(CN)_6]$ . 3H<sub>2</sub>O.

Furthermore, stability towards y-radiation of this class of compounds with possible application to radiation dosimetry will be investigated. The dyes 2 and 6 in dimethylsulphoxide showed reasonable systematic response. This prompt us to carry out further studies to understand the different factors affecting their radiolysis.

Among these factors are the concentrations of the dyes, the decoloration yield represented by G-value (which is the radiolysis yield per 100eV of absorbed energy) is to be measured under different conditions. The color stability and the radiation response of the dyes under the different conditions are to be determined.

Dye i

2-(p-N, N'-dimethylamino styryl) pyridine Ethiodide.

Dye 2

$$Me_{2}N \longrightarrow CH = C - C$$

$$N \qquad C$$

4-(p-N, N'-dimethylamino benzylidine)-2-phenyl-oxazol-5-one.

Dye 3

MeO 
$$\longrightarrow$$
 CH = C  $\longrightarrow$  C  $\bigcirc$  C  $\bigcirc$ 

4-(p-Methoxy benzylidine)-2-phenyl-oxazol-5-one.

Dye 4

HO 
$$\longrightarrow$$
 CH = C  $\longrightarrow$  C

4-(p-hydroxy benzylidine)-2-phenyl-oxazol-5-one.

Dye 5

p-Cyano p'-Valeroyl stilbene.

Dye 6

$$Me_2N \longrightarrow CH = CH \longrightarrow CH = C \longrightarrow C$$

$$N \longrightarrow C$$

$$C$$

4-(p-N, N'-dimethylamino cinnamaylidine)-2-phenyl-oxazol-5-one.