

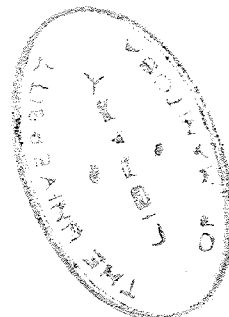
Kinetics of Luminescence Quenching
In Liquid Scintillators

by

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ABSTRACT

The kinetics of luminescence quenching in liquid scintillator solutions containing dissolved oxygen have been studied. The mechanisms involved in the quenching process can be either static or collisional. According to the experimental data for the systems investigated, the quenching process is found to be a collisional one and the kinetics of this collisional process may be explained by use of the Stern-Volmer equation. Using the Stern-Volmer equation, the quenching constants have been evaluated for the solutions and using the quenching constants, the rate constants have been evaluated and compared with rates of collision obtained from simple kinetic theory approximation. Such a comparison indicates an extremely efficient collisional mechanism with almost every collision effectively deactivating the solute molecule during its lifetime.

The effect of gases other than Oxygen have been investigated. Gases like Sulphur Dioxide exhibit almost total quenching of luminescence whereas gases like Hydrogen and Nitrogen do not exhibit quenching properties. The effect of change of solution viscosity on the quenching constant and rate constant were also investigated. As predicted by the encounter theory, both the quenching constant and the rate constant are inversely proportional to the solution viscosity. The increased viscosity of the solution causes a decrease in the collisional quenching process.

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INTRODUCTION

Kinetic studies carried out by Bowen¹⁻² on the fluorescence quenching of solutions and vapors by gases like O₂ and SO₂ showed that the process could be explained by an extremely rapid and efficient collisional mechanism. Although there are some differences between the fluorescence and scintillation processes, the similarity between the two warranted a similar investigation on liquid scintillators. This would be of both theoretical and practical value in view of the important discovery made by Pringle³ et al. that dissolved O₂ gas caused a considerable decrease in the efficiency of liquid scintillator solutions. Up to now, no quantitative measurements had been made on the O₂ quenching and no quantitative relation had been established for this quenching effect.

It is important that one distinguish between internal and external quenching processes. In the first case, the degradation of the incident energy in a solution is achieved by solvent and solute molecule interaction. In the second case, the non-emissive degradation is achieved by the interaction of the fluorescent molecules with some foreign molecules like O₂ gas. Some mention of the ideas of internal quenching will be made later. In this investigation, the most important quenching process is the external quenching of liquid scintillators by gases such as O₂ or SO₂.

In addition to the quantitative measurements of O₂ quenching and the establishment of a suitable mechanism for the quenching process in liquid scintillators, the effect of viscosity was also investigated according to the modern encounter theory. The effect of other gases on the luminescent output of liquid scintillators was checked as well.

HISTORICAL

Nuclear reactions occur with the emission of energetic particles, radiation, or a combination of both. In order to be able to characterise these particular phenomena, some means must be used to determine the energy associated with the particles and radiation. When a charged particle passes through matter, it causes excitation and ionisation of the molecules of the medium. It is the ionisation which is the basis of nearly all the methods used for the measurement and detection of such particles. In the case of uncharged radiation such as gamma rays or X-rays, the secondary ionising particles serve to characterise the radiation which produced them.

When the charged particle or radiation hits certain liquids or solids known as phosphors (luminescent materials), part of the energy is lost in molecular excitation and ionisation and may then be emitted as U. V. or visible light. The observation and the counting of these light pulses is the basis of the scintillation counter. The classical example of the scintillation counter was the activated ZnS screen used by Rutherford in his experiments with alpha particles. In this instance, the light pulses produced by the alpha particles were observed and counted with the aid of a microscope in a darkened room. A counter of this type would be insensitive to beta and gamma rays because of the weak ionisation produced in the thin phosphor screen. As a result, the scintillation counter dropped into relative disuse after this time and the Geiger-Müller type of counter was the type most widely used in the investigation of nuclear phenomena. With the development of efficient photo multiplier tubes of high gain and good sensitivity to small light intensities the interest in scintillation counters became quite pronounced. A very important advance in this field was made by Kallmann⁴ who found that a large crystal of naphthalene could be used to detect the

scintillations produced by beta and gamma rays. Then, Bell⁵ showed that a crystal of anthracene was even better since it yielded a pulse whose amplitude was five times that of a comparable naphthalene crystal. The work of Hofstadter⁶ showed that a crystal of NaI, activated by thallium, gave pulses even larger than those from anthracene. Reynolds, Harrison and Salvini⁷ were able to show that certain organic solutions emitted pulses, under suitable excitation, which were comparable in magnitude to those obtained from an anthracene crystal. Thus, these organic scintillating solutions could be used as gamma ray detectors with an efficiency relatively the same as anthracene. With these initial important discoveries, the technique involving liquid scintillators has steadily advanced until today, liquid scintillators are used in many and various fields. Indeed, there are numerous problems which, as far as the physicist is concerned are over once a suitable solution is found. For a chemist, however, they present a very interesting piece of work since some of the problems - particularly the quenching of the mechanism of light emission - can be explained along the lines of modern chemical theories.

Inorganic Scintillators

There are two main classes of scintillators - inorganic and organic. Historically, ZnS is the most interesting of the phosphors since various forms of the substance were used in the earliest visual scintillation counters. However, at the present time, its use is somewhat curtailed due to the inability to prepare crystals of large dimensions. The most important group of inorganic phosphors is the Alkali Halides. The high density of crystals such as NaI, KI and RbI makes them very efficient absorbers of electromagnetic radiation. A point of interest is that these crystals must be impregnated with an "impurity" - usually thallium. This thallium activation is found

necessary in order for the crystal to function as a suitable detector. The theories which have been put forward to explain the processes by which the crystal emits energy and the role that the activator plays in the process are too complicated and advanced for an introduction such as this. However, Curran⁸ gives an excellent account of the present theories of the luminescence of ionic solids and their properties.

Organic Crystal Scintillators

The other important group of scintillators are the large number of organic compounds. The organic group of scintillators may be divided into three classes: organic crystals, plastic scintillators and liquid scintillators. Many of the ideas which have been developed for ionic crystals are applicable, with some modification, to the field of organic crystals. Plastics and liquid scintillators, on the other hand, require new theories and explanations. These will be discussed later. As far as the migration of energy is concerned, there are a number of processes which are discussed for inorganic crystals⁸. Most authors agree that the same general type of mechanism can be used to explain the migration of energy through the organic crystal lattice. The majority of the work has been done on ionic crystals, but there is reason to believe that the phenomena of luminescence are more easily explained by examination of organic crystals and liquids. Although there has been a limited study of the properties of organic crystals, there is much material available and Bowen⁹ has made use of potential energy diagrams in discussing the activation and de-activation of organic molecules.

It is found that the organic crystals, although differing markedly in structure, do, nevertheless, possess remarkable similarity. Both Bowen and Sangster¹⁰ have carried out studies on this point and the results of the latter can be summarised very briefly as follows. The best crystalline

organic phosphors are colorless and possess a high melting point. The structure is fairly simple and the molecules should possess extensive ring structure with numerous double bonds and other structures giving extended interlocked systems. In fact, it is thought that the whole emissive and absorptive process is due to the resonance of the π electrons in the benzene like ring structure of the organic scintillators. The extensive studies carried out by Sangster on a large number of compounds have led him to these conclusions. The crystals were excited by Co^{60} γ -rays and U. V. radiation as well. This latter point is of great importance since much of our knowledge about fluorescence has been due to studies using U. V. excitation.

In the case of inorganic crystals, activators had to be used. With organic crystals, no activator is necessary and stress is placed on absolute purity and freedom from imperfections. Even traces of impurity present in the crystal can cause very serious quenching. The quenching of fluorescence is discussed very fully by Bowen⁹. No attempt will be made here to give these theories or discuss their relative merits.

Plastic Scintillators

Solid solutions of fluorescent organic compounds in a suitably transparent material have been found to yield pulse heights which are relatively high compared to anthracene. The most suitable materials used at present are polystyrene and poly vinyl toluene. These plastic scintillators offer some advantages in that they may be prepared in large volumes with relative ease and may be machined or cut to a shape or size desired for some particular problem. The mechanism of energy absorption and emission has not yet been fully resolved. However, since the plastic has no definite crystalline structure, it would appear that the plastics should be grouped with liquid scintillators rather than with the ionic crystals. Since the decay times are

of the order of 10^{-9} seconds, plastics find use in systems requiring fast detection without regard to energy evaluation.

Liquid Scintillators

Organic solvents such as benzene, toluene and xylene show very weak fluorescent properties when exposed to gamma rays or other exciting radiation. However, the fluorescent excitations produced in the molecules would nearly all be quenched by internal conversion of the energy into heat. The quenching is due to some process whereby the non-excited molecules rob the excited molecules of their energy and use it up in a non-radiative process such as conversion into heat. When the solvent contains a solute like p-terphenyl, whose molecule is highly conjugated, the fluorescent excitations of the solvent molecules can be transferred to the solute before solvent quenching can set in. This transfer of energy must occur in a time which is short enough compared to the solvent quenching time. The trapped energy of the solute is then degraded to some extent; but the quantum efficiency (photons emitted / photons absorbed) - is quite high. It should be pointed out that the emission spectrum of the solution corresponds to that of the solute and not the solvent. There are a number of mechanisms which account for the energy transfer from solvent to solute and the subsequent emission process. These will be discussed in some detail at a later stage.

With the advent of the modern photo multiplier, the use of liquid scintillators has increased very rapidly. The moderate cost of the solutions and their stability makes them very attractive for use in research - particularly in nuclear physics where large volume solutions are used as particle detectors. They are readily adaptable as regards size and shape. Their emissive spectrum can be matched very closely to most commercial tubes by the addition of very small amounts of secondary solutes known as spectrum shifters.

These spectrum shifters can shift the emissive spectrum of a solution to a more favorable position when added to the solution in quantities as small as 1 part in a thousand.

The luminescence efficiency of organic solvents like benzene, toluene and xylene is very low. However, when a solid like p-terphenyl or anthracene is added to the solvent, the resulting solution has a pulse height comparable with an anthracene crystal. These primary solutes, as they are usually called, are characterised by a number of benzene-like rings being joined together thus giving rise to a highly conjugated system. The presence of double bonds and the non-localised π electrons allows resonance structures to be set up and it is thought that the mechanism of energy absorption and emission is due to the excitation and de-excitation of these electrons and their associated resonance structures. Use of a two dimensional potential energy curve has been made by Bowen in explaining the mechanism of energy absorption and emission. Although the various primary solutes are different in properties, their structural properties are very similar. They all exhibit structures in which there are double bonds and conjugation of rings yielding extended and rigid interlocked systems.

The pioneer work on liquid scintillators and the mechanisms involved was done by Kallmann¹¹ and Kallmann and Furst¹²⁻¹³. They conducted a large number of experiments using various solutes and solvents. An important discovery was that the pulse height of a solution varied with the primary solute concentration. Furthermore, there was a certain optimum concentration of primary solute which would yield the maximum pulse height. Amounts in excess or deficiency of this quantity would yield pulse heights less than the maximum. These authors state that in the case where the primary solute is in excess of the optimum value, the decrease in pulse height is due to the concentration or self-quenching effect. Besides other processes involved,

like primary solute molecules can decrease the pulse height by a non-emissive degradatory process. It was also found that the emissive spectrum of the solution was characteristic of the primary solute and not that of the solvent even with solute concentrations as low as 10^{-4} parts. Another characteristic feature of liquid scintillators is the relative ease with which the emissive spectrum of the solution can be matched to the responsive spectrum of the commercially available photo multipliers. This is achieved by the addition of compounds known as spectrum shifters. Thus, in the case of a solid, anthracene containing naphthacene as an impurity, will show an emissive spectrum displaced to the green of the naphthacene. The optimum concentrations lie in the region 0.01 - 0.1 gms. / liter of solution. The displacement of the spectrum will occur only if the fluorescent spectrum of the "contaminant" is located at longer wave lengths than that of the bulk material. A typical spectrum shifter is 2-5-diphenyloxazole (PPO). This substance can play a dual role since it acts equally well as either a spectrum shifter or a primary solute. As with the primary solute, there is also an optimum concentration of spectrum shifter.

It is known that there are certain atoms or groups of atoms which act as quenching agents. The presence of Cl_2 , COOH and NO_2 groups in a substance will suppress the fluorescence of a solution¹⁴. These atoms or atomic groups are competing with the radiative process and are able to de-activate a number of fluorescent molecules and convert the energy to heat. Another good quenching agent is O_2 gas. A typical scintillator solution will have its luminescence efficiency decreased by almost 50 percent when a fine stream of O_2 gas is bubbled through the solution. Bowen and Norton¹⁵ found that bubbling a fine stream of N_2 gas through a solution would have a marked effect on the fluorescent emission. Thus a solution which was prepared under atmospheric

conditions would yield a pulse height of 50 percent of anthracene. This value would increase to 70 percent when the solution was bubbled with N_2 for a period of 15 minutes. The quenching of fluorescence is of great importance not only from the point of obtaining high efficiency solutions, but also from the point of elucidating the mechanisms by which the process of quenching occurs. A solution, whose pulse height has been decreased by O_2 bubbling, can be returned to its former state by bubbling with N_2 a second time. The quenching of fluorescence is not confined solely to the above mentioned substances. Traces of impurities in the solvent or in the apparatus would be sufficient to cause a noticeable quenching effect. Thus it is imperative that chemicals of the highest purity be used in the preparation of liquid scintillator solutions and that the apparatus used in the investigations be scrupulously clean.

Analogy With Fluorescence

Fluorescence of solutions has been known for a long time. One of the earliest references made was by Boyle who gave detailed instructions on how to prepare aqueous solutions. Stokes was able to show that the phenomenon depended upon absorption and re-emission at a different wave length. Fluorescence, like the light produced from a liquid scintillator, is one of the effects of interaction between light or energetic particles with matter. The emission of energy in both cases may be explained by the use of potential energy diagrams. Liquid scintillator solutions do show strong fluorescence when exposed to U. V. radiation whereas substances which exhibit fluorescent properties are not, in most cases, capable of acting as scintillators when dissolved in solution. Most authors agree that although there are a number of differences between the fluorescence and scintillation processes, there are nonetheless certain similarities as well. The fluorescence process and

the scintillation process can be distinguished by the fact that the latter's emissive process is caused by a single event in the solution or crystal. Another point of importance is that the decay time of the scintillation process is of the order of 10^{-9} seconds. Because of this and the weak intensity of the emitted light, a photo multiplier is needed as a detector. The study of either process will give valuable information to the other as well.

Scintillation Mechanisms

The mechanism involved in the scintillation process is given very fully by Kallmann and Furst¹²⁻¹³ in their two excellent papers on liquid scintillators. By means of fluorescent experiments, it is well known that a transport of energy through solids can occur over distances which are of the order of 100 atomic diameters. This can be done by the free electrons of the crystal or by migration of excitation energy from one molecule to another. This idea led the authors to hope that a similar process would occur in solutions. Here the energy would be transferred from the bulk material to the dissolved molecules. Because of the fact that the molecules of a liquid have such considerable freedom of motion, the fluorescence of a pure solvent would be small due to the fact that the collisions between molecules would cause a non-luminescent degradation of energy. Should the liquid contain foreign molecules which can trap the excitation energy, it may be that the excitation energy is transported to the dissolved molecules before it is quenched.

From their experiments, the authors found that the energy emitted by the fluorescent substances in a solution comes originally from the solvent. Along with the energy transported from solvent to solute, the process of quenching by solvent molecules must also be considered. When the solute is added, the transport of energy must be fast enough to avoid the process of quenching of the excitation energy by the solvent. Two additional conditions must now be

fulfilled at the solute molecule for large light emission to occur. These are: (1) the excitation energy of solute cannot be quenched too much by internal conversion or interaction with solvent molecules and (2) the concentration of the solute molecules must be low enough to avoid self quenching. The emission can be thought of as a competition between emission and quenching processes. Along with these we still have the quenching of energy by solvent, the transport of energy to the solute and the trapping of the energy by the solute molecules. The probability of transporting to and trapping the excitation energy by the fluorescent molecule is proportional to the concentration of the fluorescent molecule.

Thus, there are five separate mechanisms involved in the luminescence of solutions:

1. Trapping the excitation energy of the solvent at the fluorescent molecule;
2. Quenching of the excitation energy in the solvent;
3. Light emission of the fluorescent molecule;
4. Internal quenching at the fluorescent molecule;
5. Concentration quenching between similar molecules.

The authors consider the various probabilities of these processes. In terms of the characteristic lifetimes, we can write $1/\tau_6$ = reaction probability of quenching the excitation in the solvent, $1/\tau_4$ = reaction probability of trapping the excitation energy at the fluorescent molecules, $1/\tau_e$ = probability than an excited molecule emits light in unit time, $1/\tau_i$ = probability for internal quenching and $1/\tau_s$ = same for self quenching. Noting that τ_s and τ_i depend upon the concentration c so that $\tau_i/\tau_0 = k/c$ and $\tau_e/\tau_s = kc$ and $\tau_e/\tau_i + 1 = k''$, the emission intensity is found to be