CHAPTER II

Theory and Survey of Previous Investigations
We present in this chapter a brief discussion of the theoretical aspects of the process of energy transfer and related phenomenon in organic liquid scintillators and survey the results of previous investigators with a special emphasis on the effect of temperature, dilution and viscosity of the medium on the energy transfer phenomenon.

2.1. General Background of the Energy Transfer Phenomenon

Under high energy excitation of the scintillator system, the donor molecules get excited to various energy levels. The energy difference between the higher energy states is smaller compared to that between the first excited state and the ground state, since these electronic states are strongly coupled to the atomic vibrations of the molecules, the donor molecules excited to higher energy states return to the first excited pure electronic states by vibrational relaxation. From this state of the donor molecules the excitation energy passes on to the acceptor molecules which eventually results in the fluorescence emission of the acceptor molecules during the process of de-excitation of these molecules to their ground states.

It was Kallmann and Furst (Kallmann and Furst 1950, 1951, Furst and Kallmann 1952) who pioneered the study of energy transfer and related processes in scintillator systems.
using high energy radiation to excite the donor molecules. Cohen and Winreb (1954) demonstrated the energy transfer process under ultraviolet excitation of the scintillator systems, thereby eliminating many complexities of the processes accompanying high energy radiation.

2.1.1. Basic Processes in the Scintillator Systems:

In a binary organic liquid scintillator system consisting of an aromatic donor molecule, X, and a mole fraction of an organic acceptor molecule, Y, the steady state excitation of the donor molecules leads to the fluorescence emission of the acceptor molecules. The fluorescence efficiency depends not only on the molecular properties of its constituents but also on the sequence of various photophysical processes, that take place between the process of excitation of the donor molecules and the subsequent emission of radiation by the acceptor molecules. A brief account of these various intermediate processes is given in the following paragraphs.

(a) Radiative Emission:

When the incident radiation dissipates its energy in a liquid scintillator, the donor molecules get excited and then these may return to the ground state by emitting
radiation. This process is environment dependant and, in the case of many of the scintillator donors, it is negligibly small.

(b) Non-Radiative Emission:

An excited donor molecule may get de-excited leading to the conversion of excitation energy into heat. This process is known as internal conversion. Another possibility is that an excited donor molecule may collide with another donor molecule and get de-excited converting the excitation energy into heat. This process is known as concentration quenching. These processes greatly influence the efficiency of the scintillator system.

(c) Radiative Migration:

An excited donor molecule by emitting a photon may attain its ground state. The emitted photon may in turn be re-absorbed and re-emitted and this process of re-absorption and re-emission may take place a number of times and thus the excitation energy may migrate radiatively from one molecule to the other of the same species in the bulk of the medium. This self absorption process occurs only if the absorption and emission spectra of the donor molecule overlap each other considerably.
(d) Non-Radiative Migration:

Without the emission and absorption of a photon through resonance, multipole-multipole (e.g., octupole-octupole) interaction or through short lived excimer intermediates or exchange interaction the excitation energy of the donor molecules may migrate in the bulk of the donor.

(e) Radiative Transfer:

Since the first excited state of the acceptor molecule is lower than that of the donor molecule, by virtue of the overlap of the donor emission spectrum on the acceptor absorption spectrum, the radiation emitted by an excited donor molecule may be reabsorbed by the acceptor molecule over a huge intermolecular distance. However, it is experimentally known that this process can take place only at low acceptor concentrations; but at the concentration (10^{-2} M) used in practical scintillator solutions, it is negligibly small (Birks and Conte, 1968).

(f) Non-Radiative Transfer:

Through long-range coulombic (i.e., dipole-dipole and higher multipole) interaction or short-range collisional or exchange interactions, an excited donor molecule without emitting radiation may transfer its excitation energy to
the acceptor molecule non radiatively. This process is the one that is found to play a major role in the energy transfer process.

When an excited donor molecule transfers its energy to the acceptor molecule, the acceptor molecule will be excited to its first electronic level in which atomic vibrations are also present. The vibrational energy will be immediately transferred to the neighbouring molecules and to the other atomic vibrations. The remaining pure electronic energy of the acceptor molecule will be less than what is necessary to re-excite the donor molecule. Thus the excitation energy gets trapped in the acceptor molecule.

The excitation energy trapped in the acceptor molecule has to compete with the following two quenching processes before it is emitted in the form of radiation.

(g) Internal Quenching:

The excitation energy of the acceptor molecule is quenched either by the interaction with the surrounding donor molecules or by the internal conversion which is an inherent characteristic of the acceptor molecule.
(h) Self Quenching:

If an excited acceptor molecule interacts with an unexcited acceptor molecule due to resonance interaction, a double molecule may be formed in an excited state of the lower energy state. In this state of lower energy the two acceptor molecules may attract each other so much that the excitation energy may transform into atomic vibrations and then into heat.

A second possibility is that an excited and an unexcited acceptor molecule may form a double molecule due to resonance interaction with some binding energy. This double molecule may live until it is quenched or dissociated due to the impact of the surrounding molecules.

(i) Radiative De-excitation (acceptor):

The remaining excited acceptor molecules emit radiation. It is this process that is responsible for the observed fluorescence intensity.

2.1.2. Rate Parameters:

The various intermediate mechanisms discussed above are represented by the well known kinetic scheme (Birks and Conte, 1968), in which X and Y represent the donor and the
acceptor molecules respectively, and an asterisk denotes the excited state of the molecules.

<table>
<thead>
<tr>
<th>No</th>
<th>Reaction</th>
<th>Rate Parameter</th>
<th>Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$X + h\nu \rightarrow X^*$</td>
<td>$k_0$</td>
<td>Absorption</td>
</tr>
<tr>
<td>la</td>
<td>$X^* \rightarrow X + h\nu$</td>
<td>$k_1$</td>
<td>Radiative emission</td>
</tr>
<tr>
<td>lb</td>
<td>$X^* \rightarrow X$</td>
<td></td>
<td>Internal quenching</td>
</tr>
<tr>
<td>2</td>
<td>$X^* + X \rightarrow 2X$</td>
<td>$k_2$</td>
<td>Concentration quenching</td>
</tr>
<tr>
<td>3</td>
<td>$X^* + Y \rightarrow X + Y^*$</td>
<td>$k_3^Y$</td>
<td>Non radiative energy transfer</td>
</tr>
<tr>
<td>4</td>
<td>$Y^* + Y \rightarrow 2Y$</td>
<td>$k_4^Y$</td>
<td>Concentration quenching</td>
</tr>
<tr>
<td>5</td>
<td>$Y^* \rightarrow Y$</td>
<td>$k_5$</td>
<td>Internal quenching</td>
</tr>
<tr>
<td>6</td>
<td>$Y^* \rightarrow Y + h\nu$</td>
<td>$k_6$</td>
<td>Fluorescence emission</td>
</tr>
</tbody>
</table>

Of these reactions, the reactions (3) and (4) are to a first approximation proportional to acceptor concentration $Y$, hence, the rate constants are put as $k_3^Y$ and $k_4^Y$.

2.1.3 Kallmann and Furst Equation:

Kallmann and Furst (1950, 1951, 1952) were the first to give a general theory to account for the variation of scintillation intensity with acceptor concentration considering these various intermediate mechanisms represented in the above kinetic scheme.
If $k_Q$ is the rate of production of excited donor molecules by the incident radiation, because of the processes (1) to (3) the rate of formation of excited acceptor molecules is given by

$$\frac{k_o k_3 Y}{k_1 + k_2 + k_3 Y}$$ ...

(2.1)

where $k_o$, $k_1$, $k_2$ and $k_3$ are rate parameters.

As a result of the quenching processes (4) & (5) competing with process (6) the fluorescence intensity $I$ is given by

$$I = \frac{k_o k_3 Y}{\sqrt{k_1 + k_2 + k_3 Y}} \frac{k_6}{\sqrt{k_4 Y + k_5 + k_6 Y}}$$ ...

(2.2)

where $k_4$, $k_5$ and $k_6$ are the rate parameters. Equation (2.2) can be put as

$$I = \frac{P Y}{(Q + Y)(R + Y)}$$ ...

(2.3)

where $P = \frac{k_o k_6}{k_4}$ ...

(2.4)

$Q = \frac{k_1 + k_2}{k_3}$ ...

(2.5)

$R = \frac{k_5 + k_6}{k_4}$ ...

(2.6)

The constants $Q$ and $R$ are called the energy transfer parameter and the self quenching parameter respectively and normally they are referred to as Kallmann constants. $P$ is an arbitrary parameter dependent on the experimental geometry.
The value of $Q$ according to equation (2.5) is nothing but the ratio of the reciprocal of the decay time $\tau$ of the donor in the absence of the acceptor which is equal to $(k_1 + k_2)^{-1}$ to the energy transfer rate parameter $k_3$. Hence by knowing the value of $\tau$, $k_3$ can be determined.

Equation (2.3) gives the theoretically expected variation of scintillation intensity as a function of acceptor concentration.

Johnson and Williams (1951) developed another equation taking into account the direct excitation of the acceptor molecules by the incident radiation which was neglected by Kallmann and Furst. They developed this equation for the scintillation intensity as a function of acceptor concentration for inorganic crystals and later applied it to liquid scintillators also. This equation was verified to be true only in a specific case, whereas the equation of Kallmann and Furst being much simpler, found to be applicable in general.

An important advancement in the study of energy transfer by using monochromatic ultraviolet radiation to excite the donor molecules was made by Cohen and Weinreb (1954, 1956). They pointed out that the donor molecules can be excited to any desired excitation level and the energy transfer from that level to acceptor molecules can be studied by proper
choice of the exciting wavelength. The intrinsic transfer efficiency $\xi$, i.e., the fraction of the excited donor molecules which transfer their energy to the acceptor molecules is given by the equation

$$\xi = \frac{k_3 Y}{k_1 + k_2 + k_3 Y} \quad \ldots \quad (2.7)$$

Using Equation (2.5), Equation (2.7) can be written as

$$\xi = \frac{Y}{Q + Y} \quad \ldots \quad \ldots \quad (2.8)$$

It is obvious from Equation (2.8) that a plot of $Y/\xi$ versus $Y$ is linear, with slope equal to unity and the intercept equal to the energy transfer parameter $Q$.

This method has been adopted to study the energy transfer phenomenon by several investigators (e.g., Birks and Cameron, 1958; Bar and Weinreb, 1958; Basile and Weinreb, 1960; Berlman, 1960; Birks et al., 1961; Weinreb, 1961c, 1962a; Kato et al., 1962; Braun et al., 1963; Laor and Weinreb, 1965, 1969; Chikkur and Umakantha, 1976a, Basavarajappa et al., 1982).

2.2 Quenching:

It is a well known fact that the addition of certain substances like carbon tetrachloride, bromobenzene, and oxygen to a binary solution will diminish the fluorescence.
intensity of the dissolved molecules. Such substances are known as quenchers or poor donors. There are various quenching mechanisms viz., impurity or external quenching, concentration or self quenching and oxygen quenching. The quenching phenomenon has been studied by many investigators. (e.g., Pringsheim, 1949; Bowen and Wokes, 1953; Birks, 1964, 1970a; Seliger and McElroy, 1965; Wehry, 1967, 1973; Polacki and Kilarska, 1975; Saperstein and Levin, 1975; Badley, 1976; Lumb, 1978; Morrison and Pandey, 1983, Khwa}a et al., 1983).

2.2.1. External Quenching:

Some species of molecules when present as added impurities in the scintillator systems diminish the scintillation intensity considerably and hence the phenomenon is also referred to as impurity quenching. It is assumed that the phenomenon of quenching in liquids is due only to a short-range collision between an excited molecule and a quencher molecule and hence the external quenching in scintillator systems is described as a diffusion controlled collision process. Quenching studies using such molecules offer an important method of discriminating between the possible non-radiative energy transfer processes such as diffusion, migration and dipole-dipole interaction. Depending upon the nature of the donor, acceptor and the quencher, the quencher
may quench either the excited donor or acceptor or both the molecules.

If the air equilibrated solutions are used the following quenching reactions should also be taken into account.

\[
\begin{align*}
7a \quad X^* + Z_a & \rightarrow X + Z_a \quad k_{7a} \\
8a \quad Y^* + Z_a & \rightarrow Y + Z_a \quad k_{8a}
\end{align*}
\]

where \( Z_a \) represents the dissolved oxygen whose concentration is assumed to be constant.

Hence the expressions for \( Q \) and \( R \) in Equations (2.5) and (2.6) get modified to

\[
\begin{align*}
Q &= \frac{k_1 + k_2 + k_{7a}}{k_3} \quad \ldots \quad (2.9) \\
R &= \frac{k_5 + k_6 + k_{8a}}{k_4} \quad \ldots \quad (2.10)
\end{align*}
\]

If the added external quencher quenches both the donor and the acceptor molecules the following quenching reactions should also be accounted for.

\[
\begin{align*}
7b \quad X^* + Z_b & \rightarrow X + Z_b \quad k_{7b} Z_b \\
8b \quad Y^* + Z_b & \rightarrow Y + Z_b \quad k_{8b} Z_b
\end{align*}
\]

Here \( Z_b \) represents the molecular species of the quencher as well as its concentration. If \( I_0 \) represents the fluorescence intensity without the quencher, and \( I \) represents the
fluorescence intensity with the quencher of concentration \( Z_b \), we have,

\[
I_0 / I = (1 + \gamma_1 Z_b)(1 + \gamma_2 Z_b) \quad \ldots \quad (2.11)
\]

where \( \gamma_1 = k_{7b} / (k_1 + k_3 Y) \quad \ldots \quad (2.12) \)

if \( k_2 \) and \( k_{7b} \) are absorbed in \( k_1 \)
and \( \gamma_2 = k_{8b} / (k_5 + k_4 Y + k_6) \quad \ldots \quad (2.13) \)

if \( k_{8a} \) is assumed to be included in \( k_5 \).

Equation (2.11) is commonly known as the Stern-Volmer equation and \( \gamma_1 \) and \( \gamma_2 \) are referred to as Stern-Volmer quenching constants of the donor and the acceptor molecules respectively.

If the external quencher is a donor quencher, then \( k_{8b} \) and hence \( \gamma_2 \) is zero and Equation (2.11) reduces to

\[
I_0 / I = (1 + \gamma_1 Z_b) \quad \ldots \quad \ldots \quad (2.14)
\]

On the other hand if it is an acceptor quencher, then \( k_{7b} \) and hence \( \gamma_1 \) becomes zero and Equation (2.11) reads as

\[
I_0 / I = (1 + \gamma_2 Z_b) \quad \ldots \quad \ldots \quad (2.15)
\]

Now Equation (2.12) can be rewritten as

\[
\frac{1}{\gamma_1} = \left( \frac{k_1}{k_{7b}} \right) + \left( \frac{k_3}{k_{7b}} \right) Y \quad \ldots \quad (2.16)
\]
From equation (2.16) we see that a plot of $1/Y$ against $Y$ is a straight line with the intercept equal to $k_1/k_{7b}$ and the slope equal to $k_3/k_{7b}$. The ratio of intercept to slope is $k_1/k_3$ which is $Q$, the energy transfer parameter discussed earlier. Thus, using the donor quencher, one can determine the value of $Q$, and further, using the value of $k_1$ one can determine $k_3$ and $k_{7b}$ both.

The quenching constant $Y_1$ can also be put as

$$Y_1 = k_{7b} \tau_1 \quad \ldots \quad \ldots \quad (2.17)$$

Where $\tau_1 = 1/(k_1 + k_3 Y) \quad \ldots \quad (2.18)$

is evidently the decay time of the excited donor molecule corresponding to the acceptor concentration $Y$.

And Equation (2.13) can also be rewritten as

$$1/Y_2 = (k_5 + k_6)/k_{8b} + (k_4/k_{8b}) Y \quad \ldots \quad (2.19)$$

Again this is an equation of a straight line with intercept equal to $(k_5 + k_6)/k_{8b}$ and slope equal to $k_4/k_{8b}$. The ratio of the intercept to slope given by $(k_5 + k_6)/k_4$, is the self quenching constant $R$. Then by using the acceptor quencher one can determine the self quenching constant $R$, discussed earlier. Similarly, knowing the value of $(k_5 + k_6)$ one can determine $k_4$ and $k_{8b}$. 
The constant $\gamma_2$ can also be put as

$$\gamma_2 = k_{8B} \tau_2 \quad \ldots \quad (2.20)$$

where $\tau_2 = \frac{1}{k_5 + k_6 + k_\gamma Y}$ \ldots \quad (2.21)

Evidently $\tau_2$ is also the decay time of the excited acceptor molecules corresponding to the acceptor concentration $Y$.

External quenching studies have been made by several investigators (e.g., Umberger and Lamer, 1945; Bowen et al., 1947; Bowen and Metcalfe, 1951; Berry and Burton, 1955; Bowen and Sahu, 1959; Brown et al., 1961, 1962; Kropp and Burton, 1962; Samson, 1962; Dubois and Cox, 1963; Dubois and Van Hemert, 1964; Mullin et al., 1964; Raviart, 1966; Ware and Novros, 1966; Gorrell and Dubois, 1967; Ludwig and Amata, 1968b, Tanielian, 1968; Yquerabide, 1968b; Birks and Leite, 1970a; Kawski et al., 1971; Ware and Lewis, 1972; Nemzek and Ware, 1975; Chikkur and Umakantha, 1976c, 1978; Bray et al., 1977; Andre et al., 1978; Kawski and Ston, 1979; Lishon and Hammond, 1981; Umarjee and Chikkur, 1984, 1985).

2.2.2 Concentration Quenching

The fluorescence intensity under ultraviolet and high energy excitation measured as a function of acceptor concentration, decreases at very high concentrations as a
result of the reaction (4) becoming important and the phenomenon is usually known as concentration or self quenching. The common assumption regarding self quenching is the formation of an excited double molecule called excimer, when a resonance interaction takes place between an excited acceptor molecule and an unexcited acceptor molecule. An excimer may get de-excited through non-radiative or radiative process. Such an interaction leading to excimer formation either reduces the emission probability of the molecules or increases the quenching probability of the molecules depending upon the nature of interaction leading to excimer formation. The various excimeric processes that occur in the scintillator systems may be represented by the following kinetic scheme:

9 \[ Y^* + Y \rightarrow \text{D}^* \quad \text{Excimer formation} \]
10 \[ \text{D}^* \rightarrow Y + Y + h\gamma \quad \text{Excimer dissociation} \]
11 \[ \text{D}^* \rightarrow Y + Y \quad \text{Internal quenching} \]
12 \[ \text{D}^* \rightarrow Y^* + Y \quad \text{Dissociation of excimer} \]

where \( \text{D}^* \) denotes the excimer species.

The fluorescence spectra emitted by excimer and the unassociated excited molecules are respectively termed as excimer fluorescence spectrum and the monomer fluorescence spectrum. Förster and Kasper (1954, 1955) were the first to observe the excimer fluorescence in aromatic solutions.
Formation of excimers may lead either (a) to a new emission band at longer wavelength side of the monomer spectrum or (b) to a change in the monomer fluorescence spectrum giving rise to a long wavelength component or (c) to a shift in the peak position of the monomer band towards longer wavelengths.

The formation of excimers is also observed in pure donors and is referred to as donor excimer. There is also evidence (Birks and Christophorou, 1962) for the formation of mixed excimers belonging to two different species having their first excited singlet state energies close to each other and their fluorescence spectrum is known as mixed excimer fluorescence spectrum.

Birks and Christophorou (1962) distinguished the following different cases of concentration quenching depending upon the changes in the fluorescence and/or absorption spectra of organic compounds:

(i) Concentration quenching occurs, but there is no change in either the fluorescence or absorption spectrum at high concentrations. This behaviour is ascribed to the formation of non-fluorescent unstable excimers.
(ii) The concentration quenching is accompanied by a change in the fluorescence spectrum at high concentration, indicating the formation of a new molecular species, but no change occurs in the absorption spectrum. This behaviour is ascribed to the formation of fluorescent unstable excimers.

(iii) The concentration quenching is accompanied by a change in the fluorescence spectrum at high concentration by a corresponding change in the absorption spectrum. This behaviour is attributed to the formation of fluorescent excited dimers which are stable in the ground state.

(iv) No change is observed in the fluorescence spectrum at high concentration but a change is observed in the absorption spectrum, indicating the photoformation of non-fluorescent stable dimers.

Concentration quenching has been studied by many investigators (e.g., Bowen and Norton, 1939; Furst and Kallmann, 1950, 1958; Dammars-de-Klerk, 1958; Kishore et al., 1962; Förster, 1968b; Vierosanu, 1968; Bojarski, 1971; Obyknovennaya et al., 1975, Tišilov et al., 1975; Pandya and Machwe, 1977; Bojarski et al., 1975; Bauer and Cherek, 1978, Bojarski and Grabovski, 1981). Machwe et al. (1964) investigated the effect of diffusion also on the
concentration quenching process.

2.2.3. Oxygen Quenching:

When a liquid scintillator solution is exposed to atmosphere, atmospheric oxygen dissolves in it to an extent dependant on the atmospheric pressure and the temperature of the liquid. Oxygen is known to be a very good quencher. Depending on the nature of the acceptor or the donor, oxygen interacts with the excited molecules and quenches the excitation energy either of the acceptor or of the donor or of both the molecules. It was Pringle et al. (1953) who reported first the effect of oxygen quenching. Later on, it became a subject of both theoretical and experimental investigations of many investigators (Bowen and Williams, 1939; Bowen, 1954; Berry et al., 1956; Punt and Neparko, 1956; Bar and Weinreb, 1958, Berlman, 1961a, Laustriat and Coone, 1961; Berlman and Walter, 1962, Punt and Hetherington, 1962; Ware, 1962, 1966; Weinreb, 1962b; Melhuish, 1964; Braga et al., 1966; Birks, 1970c; Jones and Siegel, 1971; Sato and Satoh, 1971; Stevens, 1971; Obyknovennaya and Cherkasov, 1972; Lewis, 1976; Witkins, 1979). The oxygen quenching phenomenon has been reviewed by Parmenter and Rau (1969), Kearns (1971) and Weinreb (1971). Reactions (7a) and (8a) discussed earlier represent the kinetic scheme of the oxygen quenching.
When dry nitrogen is bubbled into the scintillator solution, the dissolved oxygen will be bubbled out, thereby the solution will be oxygen free. This technique was first made use of by Pringle et al. (1953). Later, Ott et al., (1955) used argon in place of nitrogen for this purpose. Degassing of the scintillator solutions by other methods was reported by Birks (1964). However, Nemzek and Ware (1975) have observed that the efficiency of the bubbling method, in terms of oxygen removal, is the same as that of the freeze-pump-thaw technique (Parker and Hatchard, 1962) of degassing of the fluorescent solutions.

To understand the basic scintillation process, the oxygen free condition is a must and hence, the investigators started using the gases like nitrogen and argon for their studies.

2.3. Mechanisms of Individual Processes in the Energy Transfer Phenomenon:

We shall describe in brief the mechanisms of various individual processes by which the excited donor molecules transfer their energy to the acceptor molecules in a binary liquid system and also discuss the composite models proposed to describe the rate of the over all energy transfer process.
2.3.1. Energy Migration Process:

When a donor molecule in a liquid scintillator system is excited, the excitation energy propagates through the bulk of the donor non-radiatively by a series of successive hops from one donor to another donor molecule before it emits or transfers its energy to the acceptor molecule, instead of remaining localised on the donor molecule. We shall discuss the different mechanisms put forth by various investigators for the energy migration process in liquid scintillator systems.

A. Hypothesis of Voltz, Laustriat and Coche:

Voltz et al. (1963) proposed that the donor excitation migration is due to quantum resonance between excited and unexcited donor molecules and it is due to weak multipole-multipole interaction between the two molecules (and it is octupole-octupole interaction in alkyl benzenes). This energy migration process may be represented by the kinetic scheme:

\[
\begin{align*}
    x_1^* + x_2 & \rightarrow x_1 + x_2^* \\
    x_2^* + x_3 & \rightarrow x_2 + x_3^*
\end{align*}
\]

and so on.
Where $X_1$, $X_2$ and $X_3$ are the different molecules of the same donor species.

They defined the donor excitation migration coefficient similar to the diffusion coefficient $D$, and derived an expression for $A$ as

$$ A = \left( \frac{N}{6} \right) nR^2 \quad \ldots \quad (2.22) $$

where $N$ is the number of nearest neighbours of a molecule, $R$ the intermolecular separation distance and $n$ the frequency of energy migration between the two molecules coupled by resonance, and it is given by

$$ n = \left( \frac{4}{h} \right) uF \quad \ldots \quad (2.23) $$

where $h$ is the universal Plank's constant, $F$ the Frank-Condon factor equal to 0.1 and $u$ the resonance interaction energy.

Hence, Equations (2.22) and (2.23) can be rewritten as

$$ A = \left( \frac{2uF}{3h} \right) NRF^2 \quad \ldots \quad (2.24) $$

Since the weak multipole-multipole interaction energy is usually much smaller than the thermal energy ($kT$) of the liquid, the excitation migration due to this interaction is a non activation process. According to this hypothesis $A$ is independent of temperature.
B. Hypothesis of Birks and Conte:

Birks and Conte (1968) on the other hand proposed excimer formation and dissociation model to describe the energy migration process in which excitation migration is due to the successive excimer formation and dissociation and is represented in the following kinetic schemes:

\[ \begin{align*}
X_1^* + X_2 & \rightleftharpoons D_{12}^* \rightleftharpoons X_1 + X_2^* \\
X_2^* + X_3 & \rightleftharpoons D_{23}^* \rightleftharpoons X_2 + X_3^*
\end{align*} \]

and so on. Their consideration is that, since excimer fluorescence has been experimentally observed and since excimer binding energy is much larger than octupole-octupole and/or electron exchange interaction energy, the excitation energy migration through excimers should also be taken into account, in alkyl benzenes, along with the excitation energy migration through monomer excitation and derived an expression for the excitation migration coefficient given by

\[ \hbar = \frac{\mathbf{a}^2}{6} \bar{t} = \mathbf{a}^2 k_{DX} \frac{x}{6} (1 + k_c x) \]  

(2.25)

where \( \mathbf{a} \) is the root mean square displacement due to excimer formation, which is approximately equal to double the Van der Waals radius of the molecule.
the mean time for the formation of an excited monomer to the dissociation of the excimer,

$k_{DX}$ and $k_{XD}$ are the rates of the excimer formation and dissociation processes respectively, and

$k_e$ is the molar equilibrium constant of the excimer formation and dissociation process,

\[ k_e = \frac{k_{DX}}{k_{XD}}. \]

Georghiou and Razi Naqvi (1969) also developed a similar expression for the excitation migration coefficient based on the hypothesis of Birks and Conte.

Excimer formation and dissociation in liquids is a thermally assisted rate process characterised by an activation energy which is large compared to $kT$. Hence, the energy migration due to this process is supposed to depend largely upon temperature.

2.3.2. Förster Process:

Förster (1948, 1959, 1960a, 1965, 1968a) proposed that energy transfer from an excited donor molecule to an unexcited acceptor molecule may take place due to long-range dipole-dipole or multipole-multipole interaction between the two molecules. The long-range energy transfer due to this coulombic (dipole-dipole and higher order
multipole) interaction has also been discussed by Birks (1970a), Kellogg (1970), Mataga and Kubota (1970), Pesce et al. (1971) and Yardley (1980). Such an energy transfer is strongest in the case of dipole-dipole interaction and the probability of energy transfer through this process falls off as the sixth power of the distance between the two molecules. Förster defined a critical energy transfer distance $R_0$ for which the excitation energy transfer and spontaneous deactivation of donor molecules are of equal probability and derived the following expression as

$$k_3 = \frac{9000 \ln (10) \chi^2 \eta_X^0}{128 \pi^5 n^4 N} \int \int \int \frac{f_X(\tilde{v}) \xi_X(\tilde{v}) \, d\tilde{v}}{\tilde{v}^4}$$

where $R_0 = \frac{9000 \ln (10) \chi^2 \eta_X^0}{128 \pi^5 n^4 N} \int \int \int \frac{f_X(\tilde{v}) \xi_X(\tilde{v}) \, d\tilde{v}}{\tilde{v}^4} \ldots$  \ldots (2.26)

Here $\chi^2$, the orientation factor, is 2/3 for random directional distribution of the molecular dipole moments, $\eta_X^0$ the quantum yield of the donor in the absence of the acceptor, $n$ the refractive index of the donor, $N$ the Avogadro number, $f_X(\tilde{v})$ the spectral distribution of fluorescence of the donor measured in quanta normalized to unity on a wavenumber scale, and $\xi_X(\tilde{v})$ the molar decadic extinction coefficient of the acceptor.
Larger the value of quantum yield $\eta_x$ and larger the overlap of the emission spectrum of the donor on the absorption spectrum of the acceptor, larger would be the value of $R_0$. In typical cases the value of $R_0$ is between 20 and 100 Å. $R_0$ can also be related to the critical acceptor concentration

$$y_0 = \frac{3000}{4\pi N R_0^3} \ldots \quad (2.28)$$

The critical concentration corresponds to the average acceptor concentration of one molecule in a sphere of radius $R_0$.

It is clear from Equation (2.27) that the critical transfer distance does not depend on the lifetime of the donor excited state but depends on the quantum yield of the donor emission.

Förster process is valid only if thermal equilibrium distribution over the vibrational levels of both the donor and the acceptor molecules has been established before energy transfer takes place. Further, because of nonoverlap between the absorption and the emission spectra of the donor, energy transfer from an excited donor to another unexcited donor molecule at a distance cannot take place through Förster process.
2.3.3. Diffusion-controlled collision process:

An excited donor molecule and an unexcited acceptor molecule, due to diffusion, may come in close proximity to one another separated only by a distance equal to the sum of their molecular radii during the lifetime of the excited donor molecule. During the actual collision of the two molecules, the transfer of energy may take place from the donor to the acceptor molecule. This is a diffusion-controlled collision process and hence, obviously depends upon the temperature and viscosity of the medium.

This theory was originally developed by Smoluchowski (1917) and was further extended to bimolecular reactions by Sveshnikoff (1935, 1937) and Umberger and Lamer (1945). This phenomenon of diffusion-controlled rate processes has been reviewed by Noys (1961), Alwattar et al. (1973) and Allen and Patrick (1974).

The rate constant, $k_{3D}$, for a diffusion-controlled process such as in the case of purely diffusion-controlled collisional energy transfer is given by

$$k_{3D} = 4\pi N^* D_p \rho \frac{R}{1 + R/(D\tau_x)^{1/2}}$$

(2.29)

where $N^*$ is the Avogadro number per milli mole, $R$ the sum of the molecular radii $r_x$ & $r_y$ of the interacting partners.
X and Y, D the sum of the diffusion coefficients, \( D_X + D_Y \) of the molecules X and Y, \( T_X \) the mean life time of the excited transferring donor molecule in the absence of any acceptor molecule, and \( p \) the reaction probability per encounter. Since the term shown in the paranthesis is almost equal to unity, Equation (2.29) reduces to

\[
\kappa_{3D} = 4\pi N^D p R \quad \ldots \quad (2.30)
\]

The diffusion coefficients are usually derived from the macroviscosity of the donor medium using Stokes-Einstein relation (Stokes, 1903; Einstein, 1956), which is given by

\[
D = \frac{k T}{\eta r} \quad \ldots \quad (2.31)
\]

where \( k \) is the Boltzmann constant, \( T \) the absolute temperature, \( \eta \) the macroviscosity of the medium, \( r \) the radius of the diffusing molecule and 'a' is a constant referred to as Stokes - Einstein number which can attain two values viz.,

- \( a = 4 \) for small acceptor molecules diffusing in a liquid of larger donor molecules (Full slip)
- \( a = 6 \) for larger acceptor molecules diffusing in a liquid of smaller donor molecules (no slip)

But there are some discrepancies in Stokes-Einstein relation for measuring the diffusion coefficients. Many
investigators (e.g., Osborne et al., 1963; Osborne and Porter, 1965; Gorrell and Dubois, 1967; Mitchell and Tyrrell, 1972; Skipp and Tyrrell, 1975; Tyrrell and Watkis, 1979) have found the measured diffusion coefficients to be higher or much higher than the predicted values from Stokes-Einstein relation.

Eyring has derived from the theory of absolute reaction rates an expression for the diffusion coefficient similar to Stokes-Einstein relation where \( a \geq 1 \) (Glasstone et al., 1941).

Eyring in the case of self-diffusion coefficients proposed 'a' to be 0.5 since this leads to the prediction of higher self-diffusion coefficients than the measured values. Tyrrell (1961) proposed 'a' to be 3 to bring a better agreement between these two values.

However Expression (2.31) may still be used to obtain diffusion coefficients of molecules provided a proper choice of Stokes-Einstein number 'a' is made thus accounting for the difference between the microviscosity and macroviscosity of the donor medium (Skipp and Tyrrell, 1975; Tyrrell and Watkis, 1979). Hence Equations (2.30) and (2.31) together yield

\[
 k_{3D} = \frac{4 b N k p R T}{\eta} \]  

... (2.32)

where \( b = \frac{1}{a_x r_x} + \frac{1}{a_y r_y} \)  

... (2.33)
\(d_X\) and \(d_Y\) are the Stokes-Einstein numbers for the donor \(X\) and the acceptor \(Y\) respectively. Equation (2.32) may be considered to describe the rate of diffusion controlled collision process as a function of temperature and viscosity.

2.4. Energy Transfer Models:

In any real binary solution the transfer of electronic excitation energy from an excited donor molecule to an unexcited acceptor molecule is due to the contribution of all the three processes, excitation energy migration in the donor, to different relative extents, long-range energy transfer through Forster process, and diffusion of donor and acceptor molecules. Different theoretical models, taking into account of the effect of these processes on the overall energy transfer process, have been put forth by Voltz et al. (1966), Birks and Conte (1968) and Birks et al. (1971). We shall discuss in the following pages the views of Voltz et al., Birks and Conte and Birks et al. and present their proposed models to describe the rate of the overall energy transfer process in liquid scintillator systems.

2.4.1. Voltz, Laustriat and Coche Model (VLC Model):

Voltz et al. (1966) proposed that the transfer of excitation energy of an excited donor molecule to an unexcited
acceptor molecule in the scintillator systems is non-collisional and hence takes place through the long-range resonance dipole-dipole interaction (Förster process) between the two molecules aided by diffusion and energy migration processes. They ascribed energy migration to resonance octupole-octupole interaction between the excited and the unexcited neighbouring donor molecules. Extending the ideas of Belikov and Galanin (1958) on the rate of a diffusion-controlled long-range energy transfer, Volts et al. formulated their expression to narrate the overall rate of energy transfer as,

\[ k_{3V} = 2\pi N (D + \Lambda) R_Q \]  \hspace{1cm} \text{(2.34)}

where \( N \) is the Avogadro number, \( D \) is the sum of the diffusion coefficients \( D_x \) and \( D_y \) of the donor and the acceptor molecules respectively, \( \Lambda \) is the migration coefficient and \( R_Q \) is the Förster critical energy transfer distance which can be calculated according to Equation (2.27).

2.4.2 Birks and Conte Model (BC Model):

Birks and Conte (1968) on the other hand, proposed that the transfer of excitation energy from an excited donor molecule to an unexcited acceptor molecule in the scintillator systems is a collisional interaction between the two molecules with unit transfer probability per encounter, aided
only by the processes of diffusion and energy migration. They attributed energy migration to the successive excimer formation and dissociation process in liquid systems. They formulated from the theory of diffusion controlled collision process, an expression to describe the overall rate of energy transfer as,

\[ k_{3B} = 4\pi N(D + A)pR \quad \ldots \quad (2.35) \]

where \( p \), the probability of energy transfer per encounter and is unity, \( N, D \) and \( A \) have the same meaning as in Equation (2.34) and \( R \) is the sum of the molecular radii \( r_X \) and \( r_Y \) of the donor and the acceptor molecules respectively.

When an external quencher is used to quench the excited donor molecules, only the quenching rate constant is also governed by diffusion and migration through a collision process with probability \( p \) which may be unity or less than unity, depending upon the nature of the quencher and the donor molecules. Hence, the rate constant may be expressed to describe the rate of quenching process as,

\[ k_{7bB} = 4\pi N(D + A)pR \quad \ldots \quad (2.36) \]

in which \( N, D, A \) and \( R \) have the same meaning as in Equation (2.35).
2.4.3. Donor Excitation Radius Models

Birks et al (1971) proposed one more model to account for the overall energy transfer and quenching from an excited donor molecule to an unexcited acceptor molecule in the scintillator systems in which the displacement of the donor excitation is due to simple molecular diffusion ($D_X$) but the interaction radius $r_X$ of the excited donor molecule exceeds its molecular radius $r_X$. This model holds true only in the temperature range of $-20^\circ$ to $+50^\circ$C. The model is expressed in the following form as,

$$K_3 = 4\pi N \left[ \frac{r_Y}{r_X} + \frac{1 + R(t)}{2} \right] (D_Y + D_X) \quad (2.37)$$

where $R(t)$ is a temperature dependent parameter describing the delocalization of the donor excitation.

$R(t) = 2$ is consistent from $-20^\circ$ to $+50^\circ$C. But $R(t)$ is expected to decrease above some critical temperature $t_1$ towards $R(t) = 0$ at a second critical temperature $t_2$. If this decrease of $R(t)$ with increase in $t$ is more rapid than the corresponding increase in $D_Y$ and $D_X$, the temperature dependance of $k_3$ is predicted to exhibit the following behaviour in different temperature regions:

1. $t \ll t_1 \quad (R(t) = 2), \quad k_3$ increases with $t$ as observed from $t = -20^\circ$ to $+50^\circ$C.
2. \( t_1 < t < t_2 \) \((2 > R(t) > 0)\), \( k_3 \) decreases with increase in \( t \) due to the decrease of \( R(t) \) exceeding the increase of \( D_y \) and \( D_x \).

3. \( t > t_2 \) \((R(t) = 0)\), \( k_3 \) increases with \( t_2 \), due to the increase of \( D_y \) and \( D_x \).

In this region \( k_3 \) corresponds to diffusion controlled collisional process.

2.4.4. Donor Excitation Migration Model (Birks, Najjar and Lumb, 1971):

The behaviour can alternatively be described by an expression of the form

\[
k_3 = 4\pi N (r_y + r_x) \int \left[ D_y + D_x \right] \left( 1 + \Lambda(t) \right) \text{...} \quad (2.38)
\]

where \( \Lambda(t) \) is a temperature dependant parameter describing an effective increase in \( D_x \) due to donor excitation migration.

However, radius model and donor excitation migration model explain the observed experimental results of other investigators, only qualitatively (Levin et al., 1968).
2.4.5 A Compact Model Based on Voltz et al. and Birks and Conte Models:

Though the models proposed by Voltz et al. and Birks and Conte differ from each other in the basic mechanisms involved in energy migration as well as transfer processes, they can be combined into a single equation without affecting the basic properties of the models, which can explain both energy transfer and quenching processes. Combining expressions (2.34), (2.35) and (2.36), we have formulated a compact equation (Umarjee and Chikkur, 1985) as,

\[ k_3 \text{ or } k_{7b} = 4 \pi N' (D + \Lambda) \rho R_{\text{eff}} \quad \ldots \quad (2.39) \]

where \( R_{\text{eff}} = \frac{R_0}{2} \) ; VLC Model

\[ = R_{XO} \] ; BC Model

and \( D = D_{XY} \) (i.e., \( D_X + D_Y \)), \( \rho = \rho_{XY} \) for \( k_3 \)

and \( D = D_{XO} \) (i.e., \( D_X + D_Q \)), \( \rho = \rho_{XQ} \) for \( k_{7b} \).

We have analysed our experimental results in the light of the compact Equation (2.39) in this thesis, to investigate the mechanisms involved in the processes of energy transfer and quenching, as a function of temperature, dilution and viscosity.

There are various other models to describe the energy transfer phenomenon (e.g., Förster, 1948; Belikov and Galanin, 1958; Bagdasaryan and Muler, 1965; Feitelson, 1966a;
2.5. Survey of Previous Experimental Investigations

The phenomenon of energy transfer and quenching has been a subject of intensive scientific investigation over the last 35 years and many a number of investigators have studied this phenomenon under different modes of excitations, viz., high energy radiation and ultraviolet excitation. Though many researchers have put forth their own theories to probe into the mechanisms involved and many have used these theories to interpret the mechanisms, the problem of energy transfer is still an unsolved problem in physical sciences. Because of its practical applicability the field is drawing the attention of many investigators all around the globe who have so far come a long way in the field to exhume the mystery involved in it. Even now there is a diverse opinion amongst the researchers about the process of energy transfer. Since, it is influenced by molecular aggregation, environment, temperature and viscosity of the medium, many researches were and being conducted by varying one or many of these parameters to throw more light on this phenomenon. We shall summarize in brief in the following pages the main conclusions of those investigators (e.g.,

In the very beginning of the latter part of this century, Kallmann and Furst (1950) investigated the effect of dilution on the scintillation efficiency of few scintillator...
systems under high energy radiation and observed absolutely no change in the scintillation efficiency of the Carbazole-xylene system which was diluted ten times by the addition of liquid paraffin, but later, in the terphenyl-xylene system the intensity decreased with increasing dilution. They attributed it to the internal quenching process which plays an important role in deciding the scintillation efficiency.

Later, Cohen and Weinreb (1956) while studying the effect of dilution, on two scintillator systems, viz., terphenyl-toluene and anthracene-toluene with cyclonexane as a diluent under ultraviolet excitation observed no change in the transfer efficiency, apart from a slight initial decrease at a low dilution factor, and on the basis of the scintillator concentration, they computed the critical transfer distance which was much larger than the critical transfer distance calculated on the basis of Förster's theory. On the basis of these results Cohen and Weinreb concluded that the energy migration is negligibly small but the transfer of energy may still occur through long-range dipole-dipole interaction facilitated by the diffusion process. Later, Bar and Weinreb (1958) ascribed the initial decrease of the transfer efficiency in the experiments of Cohen and Weinreb (1956) to the varying degrees of oxygen quenching in the different dilute systems. They observed that the transfer
efficiency remained constant up to a dilution factor of about eighty only in a de-oxygenated solution of anthracene in toluene.

Nafisi-Movagher et al. (1967) noticed the negligence of appreciable acceptor absorption in the region of indirect excitation of the scintillator systems of Cohen and Weinreb (1956) for its constant energy transfer efficiency over a large dilution factor. To minimize the errors they set an upper limit of about twenty for the dilution factor and included the process of energy migration along with the process of diffusion of interacting molecules and the long-range dipole-dipole interaction to account for the high values of the donor-acceptor energy transfer rate parameter. They determined the value of the migration coefficient in p-xylene solutions at 20°C from quenching studies with indirect (via p-xylene) and direct ultraviolet excitation, which reasonably agreed with those reported for benzene and alkyl-benzenes by other investigators (viz., Voltz et al., 1964; Dillon and Burton, 1965; Braga et al., 1966; Laustriat and Coche, 1966). The migration coefficient was observed to decrease with increasing dilution and the contribution to the overall transfer due to migration was almost insignificant at the upper limit of dilution set in these experiments.

The effect of dilution on the transfer process in
diphenyl-oxazole in benzene and toluene by cyclohexane was found to affect the transfer efficiency to different degrees for different excitation wavelengths as was observed by Laor and Weinreb (1969). The transfer efficiency decreased gradually when the dilution factor increased up to about four and further dilution caused only a small additional decrease in the transfer efficiency.

Birks and Conte (1968) studying the effect of dilution on energy transfer for solutions of 2,5-diphenyloxazole in benzene, toluene, p-xylene and mesitylene observed that the excimer formation process competes very efficiently with long-range transfer so that the surrounding donor molecules act as the screen against such transfer. The dilution of the donor molecules reduces the effectiveness of the donor to the long-range transfer and also causes a reduction in the migration process. Dilution of the donor decreases the migration but increases the transfer distance, so that the transfer efficiency remains practically constant.

Laustriat and Coche (1960) in their studies on donor-acceptor energy transfer efficiency observed that the transfer efficiency was practically independent of temperature in the range 30° to 10°C and an increasingly negative temperature coefficient.

Furst et al. (1966, 1968) investigated the temperature
dependance of the parameter $P/R$ (related to self quenching) and $Q$ (related to energy transfer) in the temperature range of $20^\circ - 300^\circ C$ in the case of a few scintillator systems and ascribed the major part of the observed decrease in the transfer efficiency, with the increasing temperature, to the reduction in the donor fluorescence life time.

Levin et al. (1968a, b) in their studies on energy transfer found that their results were consistent with the migration model according to which the electronic excitation energy undergoes a series of hops among the neighbouring donor molecules followed by a short-range jump to an acceptor molecule; in the temperature range of $25-240^\circ C$. They observed that the contribution of molecular diffusion to the overall transfer, in the case of efficient donors, was quite small compared to that of energy migration, but in the case of moderate and poor donors the contribution due to diffusion was also remarkable. And also, they (Levin et al., 1971) noticed that there is a systematic decrease in the number of primary excited donor molecules from which the energy can be transferred to the acceptor molecules, with increasing temperature which was the characteristic of all the solutions investigated in their experiment.

Birks et al. (1971) studied the temperature dependence of energy transfer in the case of PPO in toluene in the
temperature range -20° - +50°C and noted that the donor excitation migration adopted by previous observers (viz., Voltz et al., 1963, 1966; Birks and Conte, 1968; Birks, 1970a, b, 1971; Klein et al., 1970) requires re-examination in the light of their results. They found that the energy transfer and quenching rate parameters were consistent with the donor excitation radius model according to which the energy transfer was due to diffusion only but not due to migration in which the interaction radius of the excited donor molecules was approximately three times the molecular radius.

Chalzel (1977) studied the fluorescence quantum yield for neat benzene and neat and dilute toluene and energy transfer from toluene and benzene to PBD in the temperature range of 20° - 160°C. None of the models proposed by Voltz et al. (1966), Birks and Conte (1968) and Levin et al. (1968b) were observed to explain satisfactorily the experimental results over the entire temperature range. He explained the results by assuming that the main mechanism of energy transfer in these systems is the diffusion assisted resonance dipole-dipole interaction, which gets saturated in those systems because of the large excitation diffusion rates. However, at higher temperatures (T > 110°C) short range or collisional interactions begin to play a more important role.
Hardwick (1957) while studying the effect of diffusion on the energy transfer process observed the fluorescence efficiency of nearly identical liquids and solid solutions in which diffusion is possible in one of the systems and impossible in the other. Hence, he concluded that the collision and the mutual diffusion of the molecules did not play a major role in the energy transfer process though the fluorescence efficiency of the solid solutions was similar to that of the corresponding liquid solutions. A larger transfer efficiency observed in the case of the solid solutions was attributed to the reduction in the quenching collisions and to the favourable molecular orientation brought about by polymerization.

Knau (1957) also arrived at the conclusion that molecular diffusion had no significant effect on energy transfer in liquid and plastic systems.

And so also, Weinreb and Avivi (1958) compared the energy transfer efficiencies of liquid and plastic solutions and attributed the greater efficiency of the liquid systems under the indirect excitation to the higher mobility of the interacting molecules and the greater efficiency of the plastic under direct excitation to the greater quenching collisions due to high mobility of the molecules in the liquid systems.
Melhuish (1963) investigated the transfer process in fluid solutions at various viscosities by changing the relative fraction of the donor components and observed that diffusion considerably influenced the transfer process. Further he remarked that an excited donor molecule diffuses in its lifetime within the critical transfer distance and then transfers its energy to an acceptor molecule. The excited donor molecules in viscous systems cannot diffuse so far during their lifetimes and hence the energy transfer is less efficient in donors of low fluidity, but for the systems where the interacting molecules are always within the critical transfer distance of one another.

Katraro et al. (1977, 1979) using lasers investigated the energy transfer in liquid and solid solutions at appreciably high temperature and observed the predominance of diffusion in liquid media while the contribution due to long-range interaction is very little in the transfer process.

Weinreb (1961a, c) studied the influence of diffusion on the transfer process by varying the viscosity of the systems by adding liquid paraffin to the systems and by varying the temperature of the systems and found that the transfer efficiency increased with increasing diffusion when due allowance was made for thermal quenching. Further, Weinreb made an important remark to distinguish between the microviscosity and macroviscosity of the donor medium when
he found a good agreement between the expected and the observed values of the transfer efficiency in a system comprising anthracene in a mixture of naphthalene and liquid paraffin, and in case of anthracene in a mixture of toluene and liquid paraffin the mechanism of dipole-dipole interaction assisted by diffusion was inadequate to account for the observed values of the transfer efficiency.

Weinreb (1962a) conducted similar experiments in the temperature and viscosity ranges, \(-10^\circ\) to \(+80^\circ\) C and 0.5 to 50 cp respectively to investigate the systems comprising PPO in toluene, in a 1:9 mixture of toluene and cyclohexane and in a mixture of 1:9 toluene and paraffin oil. The decay times of toluene were also determined in these donor media at different temperatures. He found that transfer efficiency is similar in systems of toluene and toluene+cyclohexane mixtures but considerably lower in toluene+paraffin systems. But within the indicated limits of temperature the change in the transfer efficiency of the viscous system was small compared to the difference between the values of the viscous and the non-viscous systems. These results led Weinreb to conclude that although the mutual diffusion of the interacting molecules plays a part in the transfer process, the transfer efficiency itself does not give sufficient information for a detailed elucidation of the transfer mechanism.

Further, he emphasized that the difference between micro and
Macro viscosities should also be known precisely for an understanding of the transfer phenomenon in liquid systems.

Feitelson (1966b) conducted a number of experiments for the systems consisting of alcohols of different viscosities in the range, 1.0 - 68 cp and found that the critical transfer distance was greater than that expected on the basis of Förster theory. However, a better agreement between the experimental and theoretical values was brought about when the influence of diffusional motion on the Förster dipole-dipole interaction was taken into account in the theoretical model.

Elkana et al. (1968) also investigated energy transfer on a variety of alcohols of different viscosities in the range, 0.6 - 1000 cp. The efficiency of energy transfer in all the systems was different from the value expected on the basis of the Förster theory. The transfer efficiency was considerably higher in alcohols of low viscosity than in alcohols of high viscosity. Fair agreement was found between the experimental results and those derived according to the theoretical model of the resonance dipole-dipole transfer in which diffusion had been taken into consideration.

Birks et al. (1968) also attributed the observed increase in the critical transfer distance to the effect of diffusion on the Förster transfer process while
investigating transfer phenomenon in the case of benzene solutions of anthracene and perylene.

Kawski et al. (1973) also attributed the difference between the experimental and the theoretical transfer distances, to the effect of diffusion on the Förster process in their investigations in viscous solutions by fluorescence quenching studies.

Tomura et al. (1967, 1968) studied the energy transfer from pyrene to perylene in several donors such as benzene and n-hexane and found that the energy transfer rate constant to be approximately proportional to the diffusion parameter. Hence, they concluded that the collisional interaction also plays a significant role in the transfer phenomenon in addition to the long-range dipole-dipole interaction in liquid systems.

Birks and Georghiou (1968) studied the effect of diffusion on the fluorescence decay of phenanthracene in the presence of acridine in several donors of viscosities in the range, 0.4 - 64.6 cp. The system was observed to obey Stern-Volmer kinetics at low viscosity, Förster kinetics at high viscosity and intermediate kinetics at medium viscosity. Analysis of the results on energy transfer process in terms of the Voltz et al. (1966) model was questioned in the light of those results, whereas the Birks and Conte
(1968) model was considered to describe adequately the transfer phenomenon which suitably accounts for a diffusion-controlled collision process.

Birks and Leite (1970b) investigated the effect of diffusion on the efficiency of energy transfer from naphthalene to 9, 10-diphenylanthracene in benzene, cyclohexane, cyclohexanol and in benzene-cyclohexanol mixtures. The results were in reasonable agreement with the Yokota-Tanimoto (1967) model for the effect of diffusion on the Förster dipole-dipole transfer. Further, they observed that any discrepancies with the experimental results were attributed only to errors in the diffusion coefficients and/or to the errors in the critical transfer distance. They also proposed that an extension of the Förster theory to allow for the effect of higher multipole–multipole terms in the critical transfer distance, is necessary to fully account for the observed results.

Braga et al. (1966) estimated the values of Förster critical distance for monomer and excimer transfer, in the systems consisting of 2,5-diphenyloxazole in benzene, toluene, p-xylene etc. In their studies on energy transfer considering the contribution of excimer processes to the overall transfer observed only a little difference in the values of the critical distances for monomer and excimers.
Georghiou and Munro (1971) studied the transfer phenomenon considering the excimeric contribution to the overall transfer from 1, 6-dimethyl naphthalene to 9, 10-phenylanthracene in neat and dilute systems consisting of n-heptane to different proportions. They observed that the rate parameters of monomeric and excimeric transfer are not equivalent for the whole range of monomer concentrations investigated in the experiments.

2.6. Experimental method of Evaluation of the Energy Transfer and Quenching Rate Parameters:

Photostationary or phototransient techniques are used in the experimental determination of the energy transfer rate parameter and also many other parameters of the various processes in the scintillator systems. Under the photostationary conditions, quantum efficiencies are measured, and under transient conditions, lifetime. External quenching tools are also used under both the conditions by many investigators to determine the energy transfer rate parameter and the quenching rate parameter.

In our present investigation, we have adopted the more accurate and most commonly used external quenching technique to evaluate the energy transfer and quenching rate parameters (Birks et al., 1970a; Burton et al., 1955;
Hitherto, we have briefly discussed the various theoretical aspects of the phenomenon and surveyed the experimental results of previous investigators relevant to the work presented in this thesis. The literature is vast and many monographs, reports of the international conferences and review articles are available. These are cited in the beginning of the first chapter which deals with general introduction and also in the present section.