CHAPTER II

THEORY AND SURVEY OF PREVIOUS INVESTIGATIONS
In this Chapter, we shall discuss briefly the theoretical aspects of the process of energy transfer and related phenomena in organic liquid scintillators, and survey the results of previous investigations with a special emphasis on the effects of temperature, viscosity and dilution of the medium on the transfer phenomenon.

2.1 General Background of the Energy Transfer Phenomenon

Under the high energy bombardment of the scintillator solutions, the solvent molecules of the system are excited to their higher energy states. The energy differences between the higher energy states are smaller compared to the difference between the ground and the
first electronic excited state, since these electronic states are strongly coupled to the atomic vibrations of the molecule, the solvent molecules excited to higher energy states de-excite to the first excited pure electronic singlet state by vibrational relaxation. From this state of the solvent molecules the excitation energy passes onto the solute molecules, which eventually results in the fluorescence emission of the solute molecules during the radiative de-excitation of these species to their original 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 the scintillator systems using high energy radiation to excite the solvent molecules. An important advancement in these studies was, however, made by Cohen and Weinreb (1954) who demonstrated the energy transfer process under the photoexcitation of scintillator systems, thereby eliminating many complexities of the processes accompanying high energy irradiation.

2.1.1 Basic Processes in the Scintillator Systems

Steady excitation of the solvent in a binary organic liquid scintillator system which consists of an aromatic solvent molecule, \( x \), and a mole fraction of an
organic solute molecule, Y, leads to the characteristic fluorescence emission of the solute molecules. The fluorescence efficiency of such a binary organic liquid scintillator system depends not only on the molecular properties of its constituents but also on the sequence of the various photophysical processes, that occur between the intermediate stage of excitation of the solvent and the subsequent emission of fluorescence by the solute molecules. We shall give in the following paragraphs a brief account of these various processes occurring in the scintillator systems.

a) Radiative de-excitation

An excited solvent molecule may emit a photon and return to its original ground state. This process is environment-dependent and in the case of many of the scintillator solvents the process of radiative de-excitation is, however, negligibly small.

b) Non-radiative de-excitation

An excited solvent molecule may lose its excitation energy non-radiatively i.e. without the emission of a photon by internal quenching process due to environmental interactions or by concentration quenching due to aggregation effects. This process is supposed to greatly
influence the efficiency of the scintillator systems.

c) Radiative migration

When an excited solvent molecule returns to its initial ground state by emitting a photon, this photon in turn may be re-absorbed and re-emitted. This process of re-absorption and re-emission may continue a number of times and thus the excitation energy may migrate radiatively from one molecule to the another of the same species in the bulk of the system. This 'self-absorption process' occurs only if there is a considerable overlap of the absorption and emission spectra of the solvent molecules.

d) Non-radiative migration

The excitation energy of the solvent molecules may migrate in the bulk of the solvent, without the emission and absorption of a photon. This process is considered to occur non-radiatively through weak resonance multipole-multipole (e.g. octupole-octupole) interaction or through short-lived excimer intermediates or exchange interaction.

e) Radiative transfer

When an excited solvent molecule emits radiation this radiation may be re-absorbed by the solute molecule since, the first excited state of the solute is lower than
that of the solvent molecules. This process obviously
depends on the extent of the overlap of the solvent emis-
sion and the solute absorption spectra and occurs between
huge intermolecular distances. It is experimentally known,
however, that transfer through this process is negligibly
small in scintillator systems.

f) Non-radiative transfer

An excited solvent molecule without emitting
radiation may transfer its energy to the solute molecule
non-radiatively through long-range coulombic (i.e. dipole-
dipole and higher multipole) interaction or short-range
collisional or exchange interactions. This process is
understood to be the major process of energy transfer in
the scintillator systems.

Once an excited solvent molecule transfers its
energy to a solute molecule, the solute molecule in turn
would be excited to its first electronic state. Since the
energy of this equilibrium state of the solute molecule is
obviously less than that of the first excited electronic
state of the solvent, the solute molecule cannot transfer
its energy back to a solvent molecule. It has other path-
ways to get rid of its excitation energy e.g. internal
quenching, fluorescence emission, etc.
Apart from these a few other processes may occur in the scintillator systems such as excimerization, exciplex formation, etc., and impurity quenching due to the presence of some other molecular species such as dissolved oxygen which invariably affect the fluorescence efficiency of the scintillator systems. We shall not consider here these processes in developing a general theory to describe the scintillation efficiency of a binary system. However, we shall discuss them later.

2.1.2 Rate Parameters

If \( N^* \) is the concentration of an excited species of molecules, the rate equation for its decay under the steady state conditions is given by

\[
dN^*/dt = - k N^*
\]

(2.1)

where \( k \) is described as the rate parameter for the \( N^* \) decay process, and the reciprocal of it is known as the mean lifetime, \( \tau \), of the excited species.

Analogously, many of the unimolecular as well as bimolecular processes described in the preceding paragraphs may be expressed in terms of the rate equations and such a kinetic representation of these processes with their
respective rate parameters is given by the following scheme:

In this scheme, \( X \) and \( Y \) represent respectively the solvent and the solute species as well as their concentrations. An asterisk denotes the first excited electronic state of a molecule; and \( h\nu \) a photon.

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>Rate parameter</th>
<th>Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>i.</td>
<td>( X + h\nu \longrightarrow X^* )</td>
<td>( k_0 )</td>
<td>Absorption</td>
</tr>
<tr>
<td>ii.</td>
<td>( X^* \longrightarrow X + h\nu_X )</td>
<td>( k_{FX} )</td>
<td>Radiative emission</td>
</tr>
<tr>
<td>iii.</td>
<td>( X^* \longrightarrow X )</td>
<td>( k_{IX} )</td>
<td>Internal quenching</td>
</tr>
<tr>
<td>iv.</td>
<td>( X^* + X \longrightarrow X + X )</td>
<td>( k_{CX} )</td>
<td>Concentration quenching</td>
</tr>
<tr>
<td>v.</td>
<td>( X^* + Y \longrightarrow X + Y^* )</td>
<td>( k_{XY} )</td>
<td>Non-radiative energy transfer</td>
</tr>
<tr>
<td>vi.</td>
<td>( Y^* + Y \longrightarrow Y + Y )</td>
<td>( k_{CY} )</td>
<td>Concentration quenching</td>
</tr>
<tr>
<td>vii.</td>
<td>( Y^* \longrightarrow Y )</td>
<td>( k_{IY} )</td>
<td>Internal quenching</td>
</tr>
<tr>
<td>viii.</td>
<td>( Y^* \longrightarrow Y + h\nu_Y )</td>
<td>( k_{FY} )</td>
<td>Fluorescence emission</td>
</tr>
</tbody>
</table>

Of these processes, (iv) is proportional to the solvent concentration and (v) and (vi) are to the solute concentration to a first approximation. Hence the rate constants for
these processes are put as $k_{CX}$, $k_{XY}$ and $k_{CY}$ respectively.

A. Lifetimes

The reciprocal of the rate parameter for the radiative emission process in the case of the transferring solvent molecules in an infinitely dilute, non-interacting environment, as discussed earlier, is given by

$$k_{FX}^{-1} = \tau_{FX}$$

(2.2)

$\tau_{FX}$ is generally known as the radiative or the natural lifetime of the molecule. It is the intrinsic mean lifetime of the molecule in the absence of any de-activation processes other than the fluorescence emission. On the other hand, in the case of the solvent molecules in bulk and in the absence of any solute molecules

$$k_{X}^{-1} = \tau_{X}$$

(2.3)

where

$$k_{X} = k_{FX} + k_{NX} ; \quad k_{NX} = k_{IX} + k_{CX}$$

(2.4)

$\tau_{X}$ is known as the molecular fluorescence lifetime. It is the actual or the measured lifetime of the molecules in the presence of other competing de-activation processes.
including radiative de-excitation. Similarly, in the case of the solute molecules

\[ k_{FY}^{-1} = \tau_{FY} \] (2.5)

\[ k_{Y}^{-1} = \tau_{Y} \] (2.6)

where

\[ k_{Y} = k_{FY} + k_{NY} ; k_{NY} = k_{TY} + k_{CY} \] (2.7)

B. Quantum yield

Quantum yield is defined as the ratio of total energy emitted to per quantum of energy absorbed. Hence, the quantum yield of the solvent in the absence of any solute molecules is given by

\[ \phi_{X} = \frac{k_{FX}}{k_{X}} \] (2.8)

and similarly, the quantum yield of the solute is given by

\[ \phi_{Y} = \frac{k_{FY}}{k_{Y}} \] (2.9)

It is obvious from these discussions that the natural lifetime, the fluorescence lifetime and the quantum yield
are related by the following expressions

\[ \tau_X = \tau_{FX} \phi_X \quad \tau_Y = \tau_{FY} \phi_Y \]  

The values of the quantum yields and lifetimes for several scintillator solvent and solute molecules are given by Berlman (1965), Birks and Munro (1967) and Birks (1970a), Förster (1964), Munro (1968), Ware (1971), Imhof and Read (1977) and Hamilton et al. (1978) have discussed the methods of measurements of quantum yields and lifetimes of the molecules. Studies of the dependence of quantum yield and lifetimes on environment, viscosity, temperature, etc., have also been made by many investigators (e.g. Bowen and Seaman, 1962; Weinreb, 1962a; Ware and Baldwin, 1965; Greenleaf et al. 1968; Levin et al. 1968b; Birks, 1969; Pantke and Labhert, 1972; Rathi et al. 1973; Cundall and Ogilvie, 1975; Birch and Birks, 1976; Chalzel, 1977; Rice et al. 1980; Taylor et al. 1980; Blatt et al. 1981; Politis and Drickamer, 1981).

2.1.3 Energy Transfer and Scintillation Efficiencies

The quantum efficiency of energy transfer, \( f_{RX} \), is defined as the fraction of the excited solvent molecules which transfer their excitation energy to the unexcited solute molecules. It is given by
\[ f_{yx} = \frac{k_{yx}}{k_X + k_{yx}} \]  
\[ \sigma_{yx} = \frac{k_{yx}}{k_X} \]  
\[ I_p = \frac{P'Y}{(P' + Y)(Q' + Y)} \]
where

\[ p' = \frac{k_{o_{FY}}}{k_{CY}} \]  \hspace{1cm} (2.16)

\[ q' = \frac{k_{x}}{k_{YY}} \]  \hspace{1cm} (2.17)

\[ r' = \frac{(k_{TY} + k_{FY})}{k_{CY}} \]  \hspace{1cm} (2.18)

The constant \( q' \) is inversely related to the energy transfer parameter, \( \sigma^{-}_{YY} \), and the constants \( p' \) and \( r' \) are related to the self-quenching phenomenon. \( p' \) is rather, an arbitrary parameter which depends on the experimental geometry and intensity scale; but \( q' \) and \( r' \), usually referred to as Kallmann constants, are more fundamental and are characteristic of a given binary scintillator system.

Furst and Kallmann (1952), in their initial studies have determined the values of these constants for several scintillator systems. Furst et al. (1966) have later investigated, under high energy as well as ultraviolet excitation, the temperature and viscosity dependence of these parameters for a few scintillator systems.

2.2 Mechanisms of Individual Processes in the Energy Transfer Phenomenon

We shall briefly describe the mechanisms of various individual processes which may assist and through
which the excitation energy may pass on from the excited solvent to the unexcited solute molecules in a binary system, and also discuss the composite models proposed to describe the rate of the overall transfer process.

2.2.1 Energy Migration Process

When a solvent molecule in a liquid scintillator system is excited, the excitation does not remain localized on the solvent molecule. Instead, it may propagate non-radiatively in the bulk of the solvent by a series of successive hops from one solvent to another solvent molecule prior to its subsequent emission or transfer to a solute molecule. Such an excitation migration among the solvent molecules is supposed to aid the process of energy transfer to the solute molecules. However, different mechanisms have been proposed for the energy migration process in liquid scintillator systems.

A. Hypothesis of Voltz et al.

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

\[ X_1^* + X_2 \rightleftharpoons X_1 + X_2^* \]  
\[ (2.1) \]

\[ X_2^* + X_3 \rightleftharpoons X_2 + X_3^* \], etc

where \( X_1, X_2 \) and \( X_3 \) are the different molecules of the same solvent species.

Voltz et al. defined a migration coefficient, \( \Lambda \), analogous to the diffusion coefficient, \( D \), and derived an expression for \( \Lambda \), given by

\[ \Lambda = \frac{N}{6} n R^2 = \frac{2uF}{3h} N R^2 \]  
\[ (2.19) \]

where

\( N \) is the number of nearest neighbours of a molecule,

\( R \) intermolecular separation distance,

\( n \) frequency of migration of energy between the two molecules coupled by resonance,

\( h \) Planck's constant,

\( F \) Frank-Condon factor equal to 0.1 and

\( u \) resonance interaction energy.
The weak multipole-multipole interaction energy is usually much smaller than the thermal energy \( (kT) \) of the liquid. Hence the excitation migration due to this interaction is a non-activation process. And thus, the migration coefficient \( \Lambda \), according to this model is largely independent of temperature.

B. Hypothesis of Birks and Conte

Alternatively, Birks and Conte (1968) proposed excimer formation and dissociation model to describe the energy migration process. They proposed that the excitation migration is due to the successive excimer formation and dissociation process, which may be represented by the following kinetic scheme:

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

Birks and Conte on the considerations of a three-dimensional random walk process, derived an expression for the migration coefficient \( \Lambda \), given by
\[ \Lambda = \frac{\bar{x}^2}{6 \bar{t}} = \frac{\bar{x}^2 k_{DX}}{6(1 + K_e X)} \] (2.20)

where

\( \bar{x} \)

is the root mean square displacement due to excimer formation, which is approximately equal to double the van der Waals radius of the molecule,

\( \bar{t} \)

the mean time from the formation of an excited monomer to the dissociation of the excimer,

\( k_{DX}, k_{XD} \)

rates of excimer formation and dissociation processes respectively, and

\( K_e \)

the molar equilibrium constant of the excimer formation and dissociation process.

\( i.e. \ K_e = \frac{k_{DX}}{k_{XD}}. \)

A similar expression for the migration coefficient, based on the hypothesis of Birks and Conte, has also been axiomatically developed by Georgiou and Razi Naqvi (1969).

Excimer formation and dissociation in liquids is a thermally assisted rate process characterized by an activation energy which is large compared to \( kT \). Hence, the energy migration due to this process is supposed to depend
strongly upon temperature. We shall however, discuss in some detail the excimers and the possible roles these might play in the overall energy transfer process, in later sections.

2.2.2 Förster Process

An excited solvent molecule well-separated over many molecular diameters from an unexcited solute molecule may transfer its energy non-radiatively to the solute molecule. This type of transfer of energy obviously does not involve the actual collision of the two molecules. Such a long-range transfer due to resonance dipole-dipole interaction between an excited solvent and an unexcited solute molecule has been described by Förster (1948, 1959, 1960a, 1965, 1968a) and is known as the Förster process. The long-range energy transfer due to this coulombic (dipole-dipole and higher multipole) interaction has also been discussed by Birks (1970a), Kellogg (1970), Mataga and Kubota (1970), Pesce et al. (1971) and Yardley (1980).

Förster's quantum mechanical approach to this type of energy transfer assumes a long-range weak intermolecular interaction between the excited solvent and the unexcited solute molecule. When the two states of the molecules involved in the transfer are coupled by the appropriate interaction, they become degenerate.
there exists an excited state of the solute molecule which requires exactly the same excitation energy as is available in the excited solvent molecule, excitation of one of the degenerate states leads to a finite probability that the excitation will appear in the other. This probability increases with time but falls off as the sixth power of the distance separating the two molecules. In the case of the optically allowed transitions, the dipole-dipole term contributing to the interaction is often predominant. Hence, Förster assuming this interaction between the two isolated stationary molecules in solution, derived the following expression to describe the rate of a long-range resonance energy transfer from the excited solvent to the unexcited solute molecules

\[
K_{XY}^F = \frac{9 \ln(10) \chi_X^2 \phi_X}{128\pi^5 n^4 \tau_x^6} \int_0^\infty \xi_X(\tilde{v}) \xi_Y(\tilde{v}) \, d\tilde{v} / \tilde{v}^4
\]  

\[
= \left( R_0 / r \right)^6 / \tau_x
\]  

(2.21)

where

\[
R_0^6 = \frac{9 \ln(10) \chi_X^2 \phi_X}{128\pi^5 n^4 \tau_x^6} \int_0^\infty \xi_X(\tilde{v}) \xi_Y(\tilde{v}) \, d\tilde{v} / \tilde{v}^4
\]

(2.22)

and
is defined as the critical transfer distance at which the rates of energy transfer and of spontaneous deactivation of the excited solvent molecules are equal, i.e., at which \( k_i^F Y = k_x \).

\( r \) - distance between the centers of the two molecules involved in the transfer,

\( \chi \) - a factor representing the orientation dependence of dipole-dipole interaction and in the dynamic averaging limit its value is \((2/3)^{1/2} = 0.816\),

\( n \) - refractive index of the solvent medium,

\( f_x(\tilde{\nu}) \) - spectral distribution of the solvent emission measured in quanta and normalized to unity on a wavenumber (\( \tilde{\nu} \)) scale,

\( \epsilon_x(\tilde{\nu}) \) - spectral distribution of the molar extinction coefficients of the solute species.

The transfer efficiency depends on the solute concentration. And the critical concentration, \( Y_o \), corresponding to the critical transfer distance, \( R_o \), in the case of the randomly distributed molecules, is given by the following expression
The critical concentration, $Y_Q$, may be regarded as the concentration corresponding to a transfer efficiency of seventy-six percent; and also alternatively as the concentration corresponding on average to one solute molecule in a sphere of radius $R_Q$.

It is to be noted from the expression (2.23) that the critical transfer distance does not depend on the lifetime of the solvent excited state but depends on the quantum efficiency of the solvent emission. Larger the overlap of the emission spectrum of the solvent and the absorption spectrum of the solute larger would be the value of $R_Q$ and hence the probability of transfer. The overlap relation also depicts that for efficient transfer the solute molecule must possess an excited state of slightly lower energy than that of the transferring solvent molecule.

Förster process is valid under the assumption that the thermal equilibrium among the excited states is established very rapidly relative to the intermolecular transfer. Further, because of non-overlap of the emission spectrum of the solvent and the absorption spectrum of the solute molecules energy transfer through Förster process cannot take place.
2.2.3 Diffusion-controlled Collision Process

An excited solvent molecule and an unexcited solute 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 solvent molecule. And the transfer of energy may then take place from the solvent to the solute during the actual collision of the two molecules. This is a diffusion-controlled collision process and hence, obviously depends upon the temperature and viscosity of the medium.

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

The rate constant for a diffusion-controlled process such as in the case of a purely diffusion-controlled collisional energy transfer is given by

\[ k_{D_{XY}} = 4\pi N' D_{XY} p R_{XY} \left\{ 1 + \frac{R_{XY}}{(D_{XY} T_X)^{1/2}} \right\} \]  

(2.25)
where

\[ N' \] is the Avogadro number per millimole,

\[ R_{XY} \] sum of the molecular radii, \( R_x + R_y \), of the interacting molecules \( X \) and \( Y \),

\[ D_{XY} \] sum of the diffusion coefficients, \( D_x + D_y \), of the molecules \( X \) and \( Y \),

\[ \tau_x \] mean lifetime of the excited transferring solvent molecule in the absence of any solute molecules,

\[ p \] reaction probability per encounter.

Since the transient term in the parenthesis is almost equal to unity, expression (2.25) reduces to

\[ K^D_{XY} = 4\tau'(N') D_{XY} p R_{XY} \] (2.26)

The diffusion-controlled rate process depends fundamentally on the diffusion coefficients of the interacting molecules and because of scarcity of data on the experimentally measured values, the diffusion coefficients are usually derived from the macroviscosity of the solvent medium using Stokes-Einstein equation (Stokes, 1903; Einstein, 1956) which is given by
\[ D = \frac{k T}{a \eta R} \]  
\hspace{1cm} (2.27)

where

\[ a = 4 \quad \text{for small solute molecules diffusing in} \]
\hspace{1cm} the larger solvent molecules (full slip)
\[ a = 6 \quad \text{for large solute molecules diffusing in} \]
\hspace{1cm} the smaller solvent molecules (no slip)

and

\( k \) is the Boltzmann constant,

\( R \) radius of the diffusing molecule,

\( \eta \) macroviscosity of the medium and

\( T \) temperature.

It is known, however, that Stokes-Einstein relation does not predict exact values of diffusion coefficients in many cases. Osborne et al. (1963) found that the measured diffusion coefficients of napthalene and \( \alpha \)-iodonapththalene in propylene glycol to be about three times higher than the prediction of the Stokes-Einstein relation. They choose therefore, \( a \) to be 2 in expression (2.27) to yield diffusion coefficients in better agreement with the measured values. Osborne and Porter (1965) have also observed the inexact prediction of diffusion coefficients by Stokes-Einstein relation in liquid paraffin and n-hexane mixtures. Gorrell...
and Dubois (1967) have noticed the measured diffusion coefficients of several hydrocarbons in n-hexadecane to be much higher than those predicted by the Stokes-Einstein relation. Many other instances of such inaccurate predictions of the values of diffusion coefficients by Stokes-Einstein relation are found in the experiments of Mitchell and Tyrrell (1972), Skipp and Tyrrell (1975), Tyrrell and Watkis (1979).

Eyring has derived from the theory of absolute reaction rates an expression for the diffusion coefficient similar to (2.27) where $\alpha \geq 1$ (Glasstone et al. 1941).

In the case of self-diffusion coefficients Eyring proposed $\alpha$ to be 0.5. Since, this leads to the prediction of higher self-diffusion coefficients than the measured values, Tyrrell (1961) proposed $\alpha$ to be 3 to bring better agreement between these two values.

Any disagreement between the values of experimental rate parameter of a diffusion-controlled collision process and that derived from expression (2.26) has hence, often been attributed to the inexact prediction of the diffusion coefficients of the molecules by the Stokes-Einstein relation. An exhaustive account of such cases has been given by Alwattar et al. (1973).
However, in the case of lack of data on the measured diffusion coefficients, expression (2.27) may still be used to obtain diffusion coefficients of molecules provided proper choice be made of the Stokes-Einstein number, $a$, thus accounting for the difference between the microviscosity and macroviscosity of the solvent medium (Skipp and Tyrrell, 1975; Tyrrell and Watkis, 1979). Hence, expressions (2.26) and (2.27) together yield

$$k_{XY}^D = 4 \, b \, N \, k \, p \, R_{XY} \, T / \eta$$  \hspace{1cm} (2.28)

where

$$b = 1 / a_X \, R_X + 1 / a_Y \, R_Y$$  \hspace{1cm} (2.29)

$a_X$ and $a_Y$ are the Stokes-Einstein numbers for the solvent, $X$, and the solute, $Y$, molecules respectively. Expression (2.29) may be considered to describe the rate of a diffusion-controlled collision process as a function of temperature and viscosity.

2.3 Energy Transfer Models

The transfer of electronic energy from excited solvent molecules to unexcited solute molecules in liquid systems is due to the contributions of both energy migration and transfer processes which in turn are influenced by
molecular aggregation and diffusion. Different models to describe quantitatively the transfer phenomenon taking into account the effect of these various processes and their relative contributions to the overall transfer, have been proposed by Voltz et al. (1966), and Birks and Conte (1968). We shall discuss in the following paragraphs, the views of Voltz et al. and Birks and Conte and present their proposed models to describe the rate of the overall energy transfer process in the liquid scintillator systems.

2.3.1 Voltz, Laustriat and Coche (VLC) model

Voltz et al. (1966) proposed that the transfer of energy from the excited solvent to the unexcited solute molecules in 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 attributed energy migration to resonance octupole-octupole interaction between the excited and the unexcited neighbouring solvent molecules. Extending the earlier ideas of Belikov and Galanin (1958) on the rate of a diffusion-controlled long-range energy transfer, they formulated the following expression to describe the overall rate of the energy transfer process
2.3.2 Birks and Conte (BC) Model

Birks and Conte (1968) proposed that the transfer of energy from the excited solvent to the unexcited solute molecules in scintillator systems is collisional and hence takes place through the short-range collisional interaction between the two molecules with unit transfer probability per encounter, aided by the processes of diffusion and energy migration. They attributed energy migration to the successive excimer formation and dissociation process in liquid systems. Supporting their views by a few empirical evidences, they formulated from the theory of diffusion-controlled collision process, the following expression to describe the overall rate of the energy transfer process

\[ k^V_{xy} = 2\pi N' (D_{xy} + \Lambda) R_0 \]  
(2.30)

Various other models to describe the energy transfer phenomenon may, however, include those of Förster (1948), Belikov and Galanin (1958), Bagdasaryan and Muler (1965), Feitelson (1966a), Yokota and Tanimoto (1967), Steinberg and Katchalski (1968), Levin et al.
(1968b), Birks et al. (1971), Klein et al. (1976) and Chalzel (1977). The composite models proposed by Voltz et al. and Birks and Conte, necessarily have the essential features invoked to describe the energy transfer phenomenon in the various other models, but however differ with each other in the basic mechanisms involved in energy migration as well as transfer process. The elegance of the two models is that both are separable into two distinct parts as diffusion-controlled and migration-controlled rates in the rate constant describing the overall transfer process. Expressions (2.30) and (2.31) may be put in the unified form as

$$k_{yx} = 4\pi N' D_{xy} R_{\text{eff}} + 4\pi N' \Lambda R_{\text{eff}}$$  \hspace{1cm} (2.32)

where

$$R_{\text{eff}} \begin{cases} = R_C / 2 & : \text{VLC model} \\ = R_{xy} & : \text{BC model} \end{cases}$$

Further, if we put the sum of the diffusion coefficients as proportional to the diffusion parameter using Stokes-Einstein relation, the unified expression may be rewritten as

$$k_{yx} = 4 b N' k R_{\text{eff}} (T / \eta_1) + 4\pi N' \Lambda R_{\text{eff}}$$  \hspace{1cm} (2.33)
where $b$ is given by expression (2.29).

Expression (2.33) may be considered to describe the overall rate of the energy transfer process as a function of temperature and viscosity.

As mentioned earlier, the processes of excimer formation and quenching in the scintillator systems influence the energy transfer process, we shall discuss briefly these phenomena in the following sections.

2.4 Excimers

Excimers are physical entities which exist only while they possess electronic excitation energy and on dissipation of this energy they revert to dissociative pair of individual molecules. Hence, an excimer is defined as a dimer which is associated in an electronic state and is dissociative in its ground electronic state.

The excimer phenomenon has been discussed by Stevens (1968), Birks (1970a, 1975a), Mataga and Kubota (1970) and has been extensively reviewed by Birks (1975b) and Yakhot et al. (1979).

Since the excimerization either of the solvent or of the solute in a liquid scintillator system affects its scintillation efficiency, we shall consider some of these
aspects of excimers in the following paragraphs.

2.4.1 General

There are two types of molecular interactions which may contribute to excimer formation:

i) Exciton resonance due to dipole-dipole (or multipole-multipole) interaction between excited and unexcited molecular states; and

ii) Charge resonance, due to coulombic interaction between positive and negative molecular ion states.

The excimer states are considered to originate from mixture of exciton resonance and charge resonance states.

The fluorescence spectrum exhibited by excimers is called excimer fluorescence and the fluorescence spectrum exhibited by unassociated excited molecules is called monomer fluorescence. Förster and Kasper (1954, 1955) were the first to observe the excimer fluorescence in aromatic solutions.

Formation of excimers may lead either to:

i) a new emission band at longer wavelength side of the monomer fluorescence band or
ii) a change in the monomer fluorescence spectrum giving rise to a long wavelength component or

iii) a shift in the peak position of the monomer band towards longer wavelength region.

The temperature dependence of the rates of excimer formation and dissociation are described commonly by the following type of relation

\[ k' = k'_0 \exp\left(-\frac{W}{kT}\right) \]  

(2.34)

where

- \( k' \) rate of excimer formation or dissociation process
- \( W \) activation energy of the relevant process

The formation and dissociation of excimers are thus the processes characterized by activation energies and hence strongly depend upon temperature. Birks et al. (1963) proposed that excimer formation in solutions is a diffusion-controlled collision process.

Birks and Christophorou (1963) have also mentioned the following factors as responsible for inhibition of excimer formation in organic scintillator solutions.
i) Steric hindrance: The auxochromes in the molecule at both the ends of the interacting molecular dipoles may prevent the formation of excimers.

ii) Weakness of interaction: If the magnitude of the excimer interaction is very weak, the lowest excimeric singlet state excitation energy exceeds that of the monomer and no excimers are formed.

2.4.2 Excimer Processes in the scintillator systems

Many of the alkyl benzenes used as scintillator solvents are known to form excimers. A solvent excimer has, however, many channels to get rid of its excitation energy viz. excimer fluorescence, internal quenching, energy transfer and dissociation into an excited and an unexcited pair of individual molecules. Under the steady state solvent excitation the various excimeric processes that occur in the scintillator systems may be represented by the following kinetic scheme:
\[
\begin{align*}
\text{ix.} & \quad X^* + X \rightarrow D^* \quad k_{DX} \quad \text{Excimer formation} \\
\text{x.} & \quad D^* \rightarrow X + X^* \quad k_{XD} \quad \text{Dissociation of excimer} \\
\text{xi.} & \quad D^* \rightarrow X + X \quad k_{ID} \quad \text{Internal quenching} \\
\text{xii.} & \quad D^* + Y \rightarrow 2X + Y^* \quad k_{YD} \quad \text{Excimeric energy transfer} \\
\text{xiii.} & \quad D^* \rightarrow 2X + h\nu_D \quad k_{FD} \quad \text{Excimer fluorescence}
\end{align*}
\]

where

\[D^*\] denotes the excimer species.

If the solute molecules also form excimers it may result in the solute excimer emission and in the self quenching of the scintillator solutions.

Under photostationary conditions as both the monomeric and the excimeric species are present, the rate parameter of a specific photophysical process in the scintillator system is hence the weighted mean of the corresponding rate parameters of monomer and excimer processes. Under certain simplified conditions (Birks et al. 1965a) the modified expressions for the overall scintillation efficiency, the energy transfer efficiency and the energy transfer rate parameter, which are described in the earlier
sections, are given by

\[ \frac{\bar{Y}}{Y} = \frac{\bar{Y}}{X} \frac{X}{Y} (2.35) \]

\[ \bar{Y} = \bar{Y} \frac{Y}{(X + \bar{Y})} (2.36) \]

\[ = \frac{\bar{Y}}{Y} \frac{Y}{(1 + \bar{Y})} (2.37) \]

\[ \bar{Y} = \frac{(\bar{Y} + \bar{Y})}{(X + \bar{Y})} (2.38) \]

where

\[ \bar{Y} = \frac{(X + \bar{Y})}{(1 + \bar{Y})} (2.39) \]

\[ \bar{Y} = \frac{\bar{Y} + \bar{Y}}{X} = \frac{\bar{Y} + \bar{Y}}{X} (2.40) \]

\[ \bar{Y} = \frac{\bar{Y}}{X} = \frac{\bar{Y}}{X} (2.41) \]

\[ K_e \] is known as the molar equilibrium constant of the excimer formation and dissociation process. Under the assumption that \( k_{XY} \) be equal to \( k_{YD} \), it is evident from expression (2.38) that \( \bar{Y} \) reduces to \( k_{XY} \).

The various aspects of excimers have been studied by many investigators (e.g., Berlman, 1961b; Berlman and Weinreb, 1962; Ivanova et al., 1962; Birks et al., 1963;

Birks (1968a) has attributed the energy migration to the process of successive excimer formation and dissociation as has already been discussed earlier, and also postulated a model to describe the overall energy transfer process considering the contribution due to excimer processes in the scintillator systems. There is, however, still disagreement over the possible roles of excimers in the energy transfer phenomenon. The interpretation of Birks has been questioned by Dillon and Burton (1965) as regard to the variety of assumptions made by Birks with respect to specific rates and other parameters. Klein et al. (1970) regard the energy migration process as being restricted by the formation of excimers which may act as transient energy traps.
2.5 Quenching

It is very common that the fluorescence of a scintillator system is diminished or extinguished due to molecular aggregation or due to the presence of some other species of molecules. A variety of processes which cause a reduction in the quantum efficiency of a scintillator system, come under the general heading known as 'quenching'. Quenching in solutions has often been termed as 'static' or 'dynamic' depending on whether it is viscosity dependent or independent. Quenching phenomenon has been discussed by many authors, (e.g. Pringsheim, 1949; Bowen and Wokes, 1953; Birks, 1964, 1970a; Seliger and McElroy, 1965; Wehry, 1967, 1973; Badley, 1976; Lumb, 1978). We shall briefly consider in the following pages the various quenching phenomena viz. concentration or self-quenching, impurity or external quenching and oxygen quenching.

2.5.1 Concentration Quenching

Fluorescence intensity of most of the scintillator systems decreases at higher solute concentrations and the phenomenon is usually known as concentration or self-quenching. Concentration quenching is a homopolar process. It is not a simple phenomenon and may occur due to several causes. It may occur due to simple collisional degradation of the excitation energy or due to forming of dimeric or
higher polymeric aggregates in solutions. Birks and Christophorou (1962) have proposed that concentration quenching is due to the formation of excited dimers i.e. excimers and distinguished experimentally four cases of concentration quenching depending on whether or not it is accompanied by changes in the fluorescence and/or the absorption spectrum with increasing concentration of the scintillator species:

i) Concentration quenching occurs, but there is no change in either the fluorescence or the absorption spectrum at higher concentration. This behaviour is attributed to the formation of non-fluorescent unstable excited dimers.

ii) The concentration quenching is accompanied by a change in the fluorescence spectrum at higher concentration but no change occurs in the absorption spectrum. This behaviour is attributed to the formation of fluorescent unstable excited dimers (excimers).

iii) The concentration quenching is accompanied by a change in the fluorescence spectrum at higher concentration and 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) Concentration quenching occurs and there is no change in the fluorescence spectrum at higher concentration, but a change occurs in the absorption spectrum. This behaviour is attributed to the photoformation of non-fluorescent stable dimers.

Concentration quenching has been studied by many investigators (e.g. Bowen and Norton, 1939; Furst and Kallamann, 1950, 1958; Dammers-de-Klerk, 1958; Kishore et al. 1962; Forster, 1968b; Vierosanu, 1968; Bojarski, 1971; Obyknovennaya et al. 1975; Tibilov et al. 1975; Pandya and Machwe, 1977; Bauer and Cherek, 1979; Bojarski and Grabowska, 1981). Machwe et al. (1964) have also investigated the effect of diffusion on the concentration quenching process.

2.5.2 External Quenching

Some species of molecules when present as added impurities in the scintillator systems quench the scintillation intensity and hence, the phenomenon is usually referred to as impurity quenching. There are various processes through which the external quenching may occur but, in organic liquid scintillator systems it is generally known to occur through short-range collisional energy
transfer between the excited molecules of the scintillator system and the unexcited quencher molecules. The external quenching in scintillator systems is hence, described as a diffusion controlled collision process.

The quencher molecules added to a scintillator system may quench either the excited solvent or the solute or both the molecules. Those quenching process may be represented by the following kinetic scheme:

xiv. \[ X^* + Q \rightarrow X + Q \quad k_{Q_x Q} \quad \text{solvent quenching} \]

xv. \[ Y^* + Q \rightarrow Y + Q \quad k_{Q_y Q} \quad \text{solute quenching} \]

where \( Q \) represents the quencher species; and also its concentration.

These processes invariably affect the quantum efficiency of the scintillator system. And under steady state solvent excitation of the scintillator systems if \( I_F \) is the relative scintillation intensity in the absence of the quencher molecules, and
the relative scintillation intensity in the presence of the quencher molecules, then

\[ \frac{I_F}{I_Q} = (1 + K_{Qx}Q) (1 + K_{Qy}Q) \]  

Expression (2.42) is commonly known as Stern-Volmer equation and \( K_{Qx} \) and \( K_{Qy} \) are called Stern-Volmer quenching constants of the solvent and the solute molecules respectively, and are given by

\[ K_{Qx} = \frac{k_{Qx}}{(k_x + k_{yx}Y)} \]  
\[ K_{Qy} = \frac{k_{Qy}}{k_Y} \]  

If the scintillator molecules form excimers and the external quencher also quenches the excimer species e.g.

\[ \text{xvi. } D^* + Q \rightarrow 2X + Q \]  

then the expressions for the quenching constants may have to necessarily include the rate parameter due to the excimer quenching processes.

Energy transfer in quenching in the scintillator systems is supposed to be purely collisional unlike the
solvent-solute energy transfer which involves the long-range interaction also in addition to many other processes. Hence it is often believed that the quenching phenomenon offers a method of experimentally distinguishing between these processes and helps in probing the nature of solvent-solute energy transfer in the scintillator systems. External quenching studies have been made by several investigators (e.g. Umberger and Lamer, 1945; Bowen et al., 1947; Bowen and Metcalf, 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; Yguerbide, 1968b; Birks and Leite, 1970a; Kawski et al., 1971; Ware and Lewis, 1972; Nemzek and Ware, 1975; Chikkur and Umakanth, 1978, 1976c; Bray et al., 1977; Andre et al., 1978; Kawski and Ston, 1979; Lishon and Hammond, 1981).

2.5.3 Oxygen Quenching

Molecular oxygen is described as the most ubiquitous quencher of the fluorescence of organic liquid scintillator systems. Dissolved oxygen is present in almost every scintillator system exposed to atmosphere, depending upon its solubility in the given solvent medium determined by external pressure and temperature. Oxygen
quenching is an impurity quenching and may occur through several mechanisms involving the specific nature of the interacting molecules. The detailed mechanisms of the process are rather complicated. However, the net result as understood is that oxygen catalyses the non-radiative processes viz. internal conversion and intersystem crossing. The oxygen quenching phenomenon has been reviewed by Parmenter and Rau (1969), Kearns (1971) and Weinreb (1971).

The dissolved oxygen in the scintillator system quenches either the solvent or the solute or both the molecules. The processes may be represented by a similar kinetic scheme as in the case of the external quenching process. Studies of oxygen quenching have been made by several investigators (e.g., Bowen and Williams, 1939; Bowen, 1954; Berry et al., 1956; Funt and Neparko, 1956; Bar and Weinreb, 1958; Berlman, 1961a; Laustriat and Coche, 1961; Berlman and Walter, 1962; Funt and Hetherington, 1962; Ware, 1962, 1966; Weinreb, 1962b; Melhuish, 1964; Braga et al., 1966; Birks, 1970c; Jones and Siegel, 1971; Sata and Satoh, 1971; Stevens, 1971; Obyknovennaya and Cherkasov, 1972; Watkins, 1979).

The quantum efficiency of a scintillator system is affected by the presence of the dissolved oxygen. It is hence necessary to expel the oxygen from the scintillator
solutions for an understanding of the basic scintillation processes under oxygen-free conditions.

Pringle et al. (1953), in the beginning, bubbled nitrogen through the scintillator solutions to get rid of the dissolved oxygen. The nitrogen, freed from any residual oxygen after passing through magnesium perchlorate and pyrogallol, was then bubbled in to the scintillator solutions to expel the dissolved oxygen. Ott et al. (1955) used argon instead of nitrogen to bubble out the oxygen from the solutions. Birks (1964) has mentioned other methods of degassing of the scintillator solutions. Nemzek and Ware (1975) have, however, observed that the efficiency of the bubbling method, in terms of oxygen removal, is same as that of freeze-pump-thaw technique (Parker and Hatchard, 1962) of degassing of the fluorescent solutions.

It is now almost customary to use inert gases like nitrogen or argon, or to use other degassing techniques to free the scintillator solutions from the dissolved oxygen to study the scintillation phenomenon under oxygen-free conditions.

2.6 Experimental Method of Evaluation of the Energy Transfer Rate Parameter

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 the transient conditions, lifetimes. External quenching tools are also used under both the conditions, to determine the rate parameter $k_{yx}$. Birks (1970a) has described the various possible ways of evaluating the energy transfer rate parameter. We shall consider here in some detail, the experimental method of Cohen and Weinreb (1956) that we adopted in our present studies to determine the energy transfer rate parameter.

2.6.1 The Method of Cohen and Weinreb

In this method the energy transfer rate parameter is evaluated by experimentally measuring the energy transfer efficiency of the scintillator systems and by using the values of the measured fluorescence lifetimes of the transferring solvent molecules. The method originally described by Cohen and Weinreb (1956) to determine the energy transfer efficiency of the scintillator systems involves successive excitation of the solvent and the solute molecules by monochromatic radiation of proper wavelengths corresponding to the respective absorption maxima of these molecular species. For the determination of the energy transfer efficiency by this method, it is assumed
that almost a complete absorption is observed by the solvent and the solute molecules in the respective absorption regions and also that the absorption by one of the species is negligible in the absorption maximum of the other. It is further assumed that the quantum efficiency of the solute molecules to be independent of the excitation energy over this wavelength range.

The excitation of the solvent molecules results in energy transfer to the solute molecules. A fraction of the excited solvent molecules which transfer their excitation energy to the solute molecules is called as the intrinsic energy transfer efficiency by Cohen and Weinreb and is denoted by $f_{yx}$. In an actual experimental set up if,

$$I_I$$

is the measured fluorescence intensity of the scintillator solution under the indirect excitation of the solute molecules i.e. when the solvent molecules are excited by a flux of incident quanta, $n_I$ of wavelength, $\lambda_1$ and

$$I_D$$

the measured fluorescence intensity, under the direct excitation i.e. when the solute molecules are excited by a flux of incident quanta, $n_D$ of wavelength, $\lambda_2$,
then

\[ I_I = A n_I \frac{f_{yx}}{\phi_y} \quad (2.45) \]

\[ I_D = A n_D \phi_y \quad (2.46) \]

where \( A \) is a constant of the experimental arrangement.

Hence

\[ f_{yx} = \left( \frac{I_I}{I_D} \right) \left( \frac{n_D}{n_I} \right) \quad (2.47) \]

But by definition, from expression (2.12)

\[ f_{yx} = \sigma_{yx} \frac{1}{1 + \sigma_{yx} y} \]

i.e.

\[ y / f_{yx} = \sigma_{yx}^{-1} y + y \quad (2.48) \]

and from expression (2.13)

\[ \sigma_{yx} = k_{yx} / k_x \]

It is obvious from the expression (2.48) that a plot of \( y/f_{yx} \) versus \( y \) is linear, with slope unity and the intercept equal to the reciprocal of the energy transfer parameter \( \sigma_{yx} \).
Thus, if we measure experimentally the energy transfer efficiency at different scintillator concentrations and also if an absolute measurement of the solvent fluorescence lifetime, $T_x$, i.e. the reciprocal of the fluorescence emission rate constant, $k_x$, is possible, then the energy transfer rate parameter $k_{yx}$ can be determined from this method under the presumed conditions. The quanta of incident fluxes at the two wavelengths may be compared by the intensities of a fluorescent system such as of aqueous solution of fluorescein sodium, the quantum efficiency of which is constant over a wide wavelength range.

The 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).

2.7 Survey of Previous Experimental Investigations

Many researchers studied energy transfer phenomenon under high energy as well as ultraviolet excitation of the molecules. There have been thus, diverse trends in these studies and external quenching probes; time-resolved
techniques are often adopted to investigate the nature of the transfer phenomenon. It has already been mentioned that energy transfer is a bimolecular process and may be influenced by molecular aggregation, environment, temperature and viscosity of the medium including the specific nature of the interacting molecules. Hence a large number of experiments have been made under the varying conditions of one or many of these physical parameters. We shall summarise in the following pages the main conclusions of such investigations which have some bearing upon the present studies and refer here only by names to the works of some of those remaining great number of researchers who have investigated the transfer phenomenon (e.g. Kallmann and Furst, 1951; Ageno and Querzoli, 1952; Reynolds, 1952; Reid, 1952; Bowen and Broclemhurst, 1953; Furst and Kallmann, 1953, 1954a, b, 1955, 1962; Bowen and Livingston, 1954; Burton and Patrick, 1954; Burton et al., 1955; Furst et al., 1955, 1957; Berry et al., 1956; Hardwick and McMillan, 1957; Weinreb, 1957; Birks and Cameron, 1958; Brown et al., 1958, 1961; Furst et al., 1958; Förster, 1959, 1960b; Lipsky and Burton, 1959; Berlman, 1960, 1962; Weinreb, 1960, 1961b, 1962b; Birks, 1961, 1968b; Birks and Kuchela, 1961; Birks et al., 1961, 1965b; Noseworthy et al., 1961; Dubois and Stevens, 1962; Kropp and Burton, 1962; Lipsky et al., 1962; Yguerabide and Burton, 1962; Wilkinson and Dubois, 1963; Bojarski, 1964; Kilin et al.

Much early in the beginning of the study of energy transfer phenomenon in organic liquid scintillator systems, Kallmann and Furst (1950) investigated the effect of dilution on the scintillation efficiency of a few scintillator systems under the high energy irradiation. They observed in the case of carbazole-xylene system which was diluted ten times by the addition of liquid paraffin that the scintillation intensity was almost as high as of the undiluted scintillator solution. But in the case of terphenyl-xylene system the intensity was observed to decrease constantly with the increase in the dilution. Kallmann and Furst explained these results considering internal quenching processes to play an important role in determining the scintillation efficiency of those systems.

Cohen and Weinreb (1956) investigated more elaborately the effect of dilution on the transfer process under the ultraviolet excitation. They observed in the case of
terphenyl-toluene and anthracene-toluene systems with cyclohexane as an inert diluent that the energy transfer efficiency remained nearly constant up to large dilution factors of hundred and four hundred respectively; apart from a slight initial decrease at low dilution factors. They estimated the values of critical transfer distance from the experimental dependence of transfer efficiency on the scintillator concentration. However, the critical transfer distances computed on the basis of Förster theory from the absorption and fluorescence properties of the interacting molecules turned out to be much smaller than the experimental values. These results led Cohen and Weinreb to conclude that energy migration is negligibly small but the transfer of energy may still occur through long-range dipole-dipole interaction facilitated by the diffusion process.

Subsequently, Bar and Weinreb (1958), studying the effect of dilution on the transfer efficiency, attributed 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. And they observed that in a de-oxygenated solution of anthracene in toluene, however, the transfer efficiency remained constant up to a dilution factor of about eighty only.
Nafisi-Movagher et al. (1967) noticed that the insensitivity of the energy transfer efficiency even to much higher dilutions of the scintillator systems in the experiments of Cohen and Weinreb (1956) was due to the negligence of appreciable solute absorption in the region of indirect excitation of the scintillator systems. Setting an upper limit of about twenty for the dilution factor, to minimize errors, they observed in their studies that the processes of diffusion of the interacting molecules and the long-range dipole-dipole interaction alone could not explain the high values of the solvent-solute energy transfer rate parameter. Hence, they proposed to include the process of energy migration to account for these large values. They determined the value of the migration coefficient in the case of p-xylene as the scintillator solvent from quenching studies, 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 increase in the dilution and the contribution to the overall transfer due to migration was almost insignificant at the upper limit of dilution set in these experiments.

Laor and Weinreb (1969) studied the effect of dilution on the transfer process in the case of diphenyl-
oxazole in benzene and toluene by cyclohexane. Dilution was found to affect the transfer efficiency to different degrees for different excitation wavelengths. 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 in scintillator systems observed that the excimer formation process competes very efficiently with long-range transfer, so that the surrounding solvent molecules act as a 'screen' against such transfer. The dilution of the solvent reduces the effectiveness of the solvent screen to the long-range transfer and also causes a reduction in the migration process. But the decrease in the migration coefficient due to dilution, however, is offset by an increase in the effective collision transfer distance from collisional to the long-range transfer.

Laustriat and Coche (1960) observed that the solvent-solute energy transfer efficiency was practically independent of temperature in the range 243-263 °K and at higher temperature the transfer efficiency had an increasingly negative temperature coefficient.

Furst et al. (1966, 1968) studied the effect of temperature on energy transfer in the range 293-573°K.
They investigated the temperature dependence of the parameters $P'$, $R'$ (related to self quenching) and $Q'$ (related to energy transfer) in the case of a few scintillator systems and attributed the major part of the observed decrease in the transfer efficiency with increasing temperature to the reduction in the solvent fluorescence lifetime.

Levin et al. (1968a, b) studied the energy transfer in the temperature range 293-513 °K and 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 solvent molecules followed by a short-range jump to a solute molecule. It was observed that contribution of molecular diffusion to the overall transfer in the case of efficient solvents was quite small compared to that of energy migration. But in the case of moderate and poor solvents the contribution due to diffusion was also remarkable.

Levin et al. (1971) investigated the temperature variation of a parameter representing the number of primary excited solvent molecules from which the energy can be transferred to the solute molecules, in the range 293-513°K. They noted that a systematic decrease in this parameter with increasing temperature was the characteristic of all
Birks et al. (1971) studied the temperature dependence of energy transfer in the case of 2,5-diphenyl oxazole in toluene in the range 253-323 K and noted that the solvent 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 rate parameters were consistent with the solvent excitation radius model according to which the energy transfer was due to only diffusion but not migration and in which the interaction radius of the excited solvent molecules was approximately three times the molecular radius.

Chalzel (1977) investigated the transfer process by measuring the energy transfer efficiency in the case of both neat and dilute scintillator systems in the temperature range 293-433 K. None of the models proposed by Voltz et al. (1966), Birks and Conte (1968), and Levin et al. (1968b) were observed to satisfactorily explain the experimental results over the entire temperature range. Chalzel observed that the results could, however, be explained by assuming the main mechanism of energy transfer to be diffusion-assisted resonance dipole-dipole interaction and that at appreciably high temperatures short-range
collisional interaction play a more important role.

Hardwick (1957) studied the effect of diffusion on the energy transfer process by observing the fluorescence efficiency of nearly identical liquid and solid solutions in which, diffusion is possible in one of the systems and impossible in the other. Since the fluorescence efficiency of the solid solutions was similar to that of the corresponding liquid solutions, he concluded that the collision and hence the mutual diffusion of the molecules did not play a major part in the energy transfer process. 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 concluded from similarities in the fluorescence behaviour of liquid and plastic systems that molecular diffusion had no significant effect on energy transfer.

Similarly, Weinreb and Avivi (1958) compared the energy transfer efficiencies of liquid and plastic solutions of similar compositions. The greater efficiency of the liquid systems, under the indirect excitation, was attributed to the higher mobility of the interacting molecules. On the other hand, under direct excitation,
the efficiency of the plastic was more compared to that of the liquid solution and this was attributed to the greater quenching collisions due to high mobility of the molecules in the liquid systems.

Melhuish (1963) investigated energy transfer from 9-methylanthracene to perylene in fluid solutions of benzene-dibutylphthalate mixture at various viscosities by changing the relative fraction of the two solvent components and observed that diffusion considerably influenced the transfer process. Melhuish further remarked that an excited solvent molecule diffuses in its lifetime within the critical transfer distance and then transfers its energy to a solute molecule. The excited solvent molecules in viscous systems, however, cannot diffuse so far during their lifetimes and hence the energy transfer is less efficient in solvents of low fluidity. But the diffusion process would not necessarily matter for systems where the interacting molecules are always within the critical transfer distance of one another.

Katraro et al. (1977, 1979) have investigated the laser induced energy transfer in liquid as well as solid solutions in appreciably high temperature ranges. They concluded that in liquid media energy transfer due to diffusion predominates and transfer via long-range
interaction contributes very meagrely to the transfer process.

Weinreb (1961a,c) studied systematically the influence of diffusion on the transfer process in the temperature and viscosity ranges, 273-353°K and 0.5-175 cp respectively. Viscosity of the scintillator systems was varied by adding liquid paraffin to the systems and by changing the temperature. In all the systems an increase in the transfer efficiency with increasing diffusion was observed when due allowance was made for thermal quenching. In the case of anthracene in a mixture of naphthalene and liquid paraffin, good agreement was found between the expected and the observed values of the transfer efficiency. Whereas, in the 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, however, made an important remark at this juncture to distinguish between the microviscosity and the macroviscosity of the solvent medium.

Weinreb (1962a) conducted similar experiments in the temperature and viscosity ranges, 263-353°K and 0.5-50 cp respectively, investigating the scintillator systems consisting of 2,5-diphenyloxazole in neat toluene, in
dilute mixture of 1:9 toluene and cyclohexane, and in 1:9 toluene and liquid paraffin. Lifetimes of toluene were also determined in these solvent media at different temperatures. It was observed that the transfer efficiency in the viscous system was lower than that in the non-viscous 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, Weinreb emphasised that the difference between microviscosity and macroviscosity should also be known precisely for an understanding of the transfer phenomenon in liquid systems.

Feitelson (1966b) investigated the transfer from p-terphenyl to 9-methylandanthracene in a number of alcohols of different viscosities in the range 1.0-68 cp. The experimental value of the critical transfer distance was found to be greater than that expected on the basis of Förster theory. Better agreement between the experimental and the theoretical results was, however, brought when the influence of diffusional motion on the Förster dipole-dipole
interaction was taken into account in the theoretical model.

Elkana et al. (1968) similarly investigated the energy transfer from naphthalene to anthranilic acid in a wide 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 to be 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, studying the transfer phenomenon in the case of benzene solutions of anthracene and perylene, attributed the observed increase in the critical transfer distance to the effect of diffusion on the Förster transfer process.

Kawski et al. (1973) investigated energy transfer in viscous solutions by fluorescence quenching studies. The difference between the experimental and the theoretical transfer distance was similarly attributed to the effect of diffusion on the Förster process.

Tomura et al. (1967, 1968) studied transfer from
pyrene to perylene in several solvents such as benzene and n-hexane. The energy transfer rate constant was found to be approximately proportional to the diffusion parameter. Hence, they concluded that 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 pentanthracene in the presence of acridine in several solvents 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 in terms of the Voltz et al. (1966) model was questioned in the light of those results, whereas the model of Birks and Conte (1968) 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 attributable 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 on the magnitude of the critical transfer distance, is necessary to fully account for the observed results.

Braga et al. (1966) studied energy transfer considering the contribution of excimer processes to the overall transfer in systems containing 2,5-diphenyl oxazole in benzene, toluene, p-xylene, etc. They estimated the values of Förster critical distance for monomer and excimer transfer and observed only a little difference in these values.

Similarly, 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 containing 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.
Hitherto, we have briefly surveyed the experimental results of previous investigators relevant to the present studies with a special emphasis on the effect of dilution, temperature and viscosity of the medium on the energy transfer phenomenon. However, a large number of experiments have also been done under the normal conditions. References to at least a cross section of those investigations are cited in the beginning of the present section and also in the general introduction of the First Chapter.