CHAPTER VI

Summary and Concluding Remarks
Finally, we shall summarise and conclude our present studies. In the present investigation, we proposed to study the process of electronic excitation energy transfer and quenching in neat and dilute organic liquid scintillator systems in the 20°C - 70°C temperature range and in the 0.6 to 40.0 cp viscosity range. The subject of the investigation was to understand the basic mechanisms involved in the overall transfer of excitation energy from the excited donor molecules to unexcited acceptor molecules and the role played by the individual processes such as energy migration, Brownian diffusion and the long-range dipole-dipole or higher order multipole-multipole interaction leading to Förster process and the basic mechanisms involved in the energy migration, namely, quantum resonance interaction between an excited donor molecule and an unexcited donor molecule and excimer formation and dissociation.

Our experimental measurements involved the determination of the quenching constant $\tau$ at different acceptor concentrations as a function of temperature for different scintillator systems. Our studies also involved the measurements of viscosity and density of different donor media at various temperatures of our interest. The measurements were also consisted of recording the absorption spectra of the scintillator acceptors at ambient temperature, in different donor media.
In the case of TC system surprisingly the Stern-Volmer plots were found to be non-linear at all acceptor concentrations and at all temperatures. This was found to be due to the interaction between the halogen group of the quencher molecule and cyclohexane. Therefore, we have used Aniline as quencher in TC system and obtained the data which are consistent with the Stern-Volmer equation. A detailed discussion of the non-linear behaviour of this system with bromobenzene as quencher is presented in the appendix.

The values of the energy transfer rate parameter \( k_3 \) and the quenching rate parameter \( k_7b \) were evaluated at different temperatures using the experimentally determined values of quenching constant \( \gamma \) and the reported values of the donor fluorescence lifetime at each of the temperatures.

The energy transfer rate parameter and the quenching rate parameter increase with temperature in the case of both the acceptors in neat toluene system and in both the dilute systems in the case of acceptor 2. These variations are in qualitative agreement with the expectation that increase in temperature facilitates the Brownian diffusion of the interacting molecules and hence, the energy transfer and quenching processes. But when we compare the values of \( k_3 \) and \( k_7b \) in TN system with the corresponding values of \( k_3 \) and \( k_7b \) in both the dilute systems at the respective temperatures, we find
that the values of $k_3$ and $k_{7b}$ in TC and TP systems are much smaller than those in TN system which may be attributed to dilution. Thus these results provide definite evidence for the role played by the Brownian diffusion of the interacting molecules in the overall energy transfer process.

The linear variation of the energy transfer rate parameter $k_3$ with the sum of the diffusion coefficients $D_{xy}$ and the linear variation of the quenching rate parameter $k_{7b}$ with the sum of the diffusion coefficients $D_{xq}$ shows that energy migration is due to the resonance interaction between an excited donor molecule and an unexcited donor molecule and evidently not due to excimer formation and dissociation, in spite of the fact that toluene is known to form excimers. A quantitative analysis of the results on the basis of the compact equation enabled a unique method of evaluation of the energy migration coefficient $\Lambda$ and the effective energy transfer distance $R_{\text{eff}}$.

It is interesting to note that the energy migration coefficient $\Lambda$ thus evaluated is independent of the assumptions regarding the final step of energy transfer made in both Voltz et al. and Birks and Conte models. The fact that the values of energy migration coefficient corresponding to $k_3$ and $k_{7b}$ are close to each other and their mean values are different in different scintillator systems, supports the
well-known assumption that the migration of energy is due entirely to the property of the transferring donor alone.

The values of effective energy transfer distance $R_{\text{eff}}$ involve the knowledge of the final step of energy transfer. It is well known that the phenomenon of quenching is due only to the interaction between the excited donor and the quencher molecules. Hence, the determination of the values of $R_{\text{eff}}$ simultaneously for both, corresponding to $k_3$ and $k_7$, helps resolve unambiguously in favour of either Voltz et al. or Birks and Conte models. In our case the values of $R_{\text{eff}}$ corresponding to $k_3$ are close to the respective values of $R_{\text{XY}}$ in TN and TC systems. And in TP system the value of $R_{\text{eff}}$ corresponding to $k_3$ is close to $R_0/2$. The higher value of $R_{\text{eff}}$ in TP system which is very close to $R_0/2$ may be understood in the following way. In TP system since liquid paraffin is a highly viscous neutral diluent, both migration and diffusion processes get hindered due to dilution and viscosity respectively, and in turn this decrease in these two processes may get compensated by the long-range energy transfer from donor to acceptor molecules due to Förster process, leading to the increase in the effective energy transfer distance $R_{\text{eff}}$. But the values of $R_{\text{eff}}$ in TC and TN systems agree with $R_{\text{XY}}$ though the dilution factors are different in both the systems. This may be understood in the following way. Though the dilution is known to decrease the
migration process, the viscosities being the same, the decrease in migration process due to dilution may be compensated by the increase in the diffusion process keeping the effective transfer distance almost unchanged without embarking the long-range transfer. Further, in all the three systems the values of $R_{eff}$ corresponding to $k_\tau$ agree with the corresponding values of $R_X\bar{Q}$ provided we adjust the values of $p_X\bar{Q}$ suitably to less than unity; since it is well-known that the value of $p_X\bar{Q}$ is less than unity, we can unambiguously conclude that the quenching process is governed in all the three systems by Birks and Conte model with probability of quenching per encounter being much less than unity.

Further, we find that the value of $p_X\bar{Q}$ is not the same in all the three systems. It is highest in TP system ($p_X\bar{Q}=0.36$), low in TN system (0.18) and least in TC system (0.06).

These results can be explained in the following way. The fact that $p_X\bar{Q}$ in TP system is about two times larger than that in TN system shows that the probability of quenching per encounter increases with viscosity. This is because, once the interacting molecules come in close contact with each other, they cannot easily separate away due to the sluggish nature of the surrounding molecules. Therefore, the probability of quenching per encounter may increase with viscosity. On the other hand, $p_X\bar{Q}$ in TN system is about three times larger than that in TC system, though the
viscosities of both the systems are almost the same. It has been observed by Tanielian (1966) in a large number of donor acceptor combinations that the values of $p_{XQ}$ depend on the nature of both the interacting molecules. Since in our case the interacting molecules in TN and TC systems are different, though the acceptor and the donor are the same, the low value of $p_{XQ}$ may be attributed to the nature of interaction between toluene and Aniline molecules in the given environment.

Hence, the quenching studies of energy transfer at different temperatures and dilution offer rich information to probe into the nature of energy transfer process. Thus our results provide concrete evidence for the facts which were largely speculative so far.

However, it is worth-while conducting the experiments at different degrees of dilution of the scintillator systems as a function of temperature, which would help us to know more about the energy migration coefficient, the effective transfer distance and any probable correlation in the behaviour of these two parameters. It is important to investigate independently the systems involving a scintillator donor which forms excimers and the other does not and compare the results of these different types of the systems. This may give a better understanding of the nature of energy
migration and transfer process. The effective transfer distance and the migration coefficients being the variable parameters, which depend on the nature of the molecular environments, may accidentally lead to some erroneous conclusions in favour of either of the models if we consider the experimental results obtained over a limited range of temperature, viscosity and dilution, for a few scintillator acceptors. Therefore, it is essential to investigate a large number of scintillator systems over a wide range of temperature, viscosity and dilution for different acceptor molecules which vary in their molecular structure, size and spectral characteristics.

We see from the analysis of the data that the values of the rate parameters $k_3$ and $k_{7b}$ depend to a large extent on the fluorescence lifetimes of the donor molecules. Hence, determination of the fluorescence lifetimes is very helpful in the determination of the rate parameters and hence the transfer process. As seen from the evaluation of the diffusion coefficients the values of 'a' in different systems are adjustable parameters. It is therefore, essential to measure the diffusion coefficients of the scintillator molecules for a definite understanding of the energy transfer phenomenon.
Lastly, we may observe that we have rather extensively studied the energy transfer process in organic scintillator systems under different environments, which has given us some in-sight into this vast and yet mysterious field. We hope, some of these studies presented in this thesis would help in future to know more about the process of energy transfer in organic liquid scintillators. An intensive study of some of the unsolved problems mentioned in this thesis is currently in progress.