CHAPTER V

SUMMARY AND CONCLUDING REMARKS
Lastly we shall summarise and conclude our present studies. To recall our scheme of investigations expressed in the introductory Chapter, we proposed to study the process of electronic excitation energy transfer in neat as well as dilute organic liquid scintillator systems in a moderate range of temperature 293–353 °K and viscosity 0.6–39.0 cP. The object of the investigation was to understand precisely the basic mechanisms involved in energy migration as well as in transfer process and the role played thereby the energy migration and the Brownian diffusion of the interacting molecules in the overall energy transfer process.
Our experimental measurements essentially involved the determination of the energy transfer efficiency as a function of temperature for different scintillator systems at various scintillator concentrations. Our studies also involved the measurements of viscosity, density and refractive index of the different solvent media and the measurement of diffusion coefficients of the scintillator molecules in some of these solvent media at various temperatures. The measurements also consisted of recording the spectral characteristics of the scintillator solutes at ambient temperature.

The values of the energy transfer rate parameter were evaluated for all the scintillator systems at different temperatures from the experimentally measured values of the energy transfer efficiency as a function of scintillator solute concentration and the reported values of the solvent fluorescence lifetime at each of the temperatures.

The energy transfer rate parameter decreases on dilution and increases with temperature in the case of both the neat as well as the dilute scintillator systems which, of course, is in qualitative agreement with the theoretical expectations of the effect of dilution and temperature on the energy transfer process. Our results thus provide evidence for the definite roles of energy migration and
the Brownian diffusion of the interacting molecules in the overall energy transfer process.

The linear variation of the energy transfer rate constant with the diffusion parameter further shows that though the transferring solvent is known to form excimers, the migration of energy is due to the resonance interaction between an excited and an unexcited solvent molecule rather than the successive solvent excimer formation and dissociation process. A quantitative analyses of our results considering the linear variation of the energy transfer rate constant with the diffusion parameter enabled a unique evaluation of the energy migration coefficient and the effective energy transfer distance $R_{\text{eff}}$. The difference between the values of the measured and the estimated diffusion coefficients on the basis of the measured macroviscosity of the solvent medium has however, been taken into account in these analyses.

Interestingly, the energy migration coefficient, thus evaluated is free from the assumptions regarding the final step in the energy transfer process as envisaged in both the BC and the VLC models. The energy migration coefficient assumes a consistent set of values in the case of each type of the scintillator systems supporting the well-known observation that the migration of energy is
due entirely to the property of the transferring solvent alone.

The observed effective energy transfer distance $R_{\text{eff}}$ involves the knowledge of the final step in the mechanism of the energy transfer process. But, a set of experimental values of $R_{\text{eff}}$ obtained from the analyses of our results in the case of each type of the scintillator systems help to resolve unambiguously in favour of neither the BC nor the VLC models. As $R_{\text{eff}}$ is markedly different in different types of the systems and varies in magnitude on solution, it was regarded as only an effective transfer distance over which an excited solvent molecule transfers its energy to an unexcited solute molecule in the final step of energy transfer process in a given environment. The observed change of $R_{\text{eff}}$ in the different types of the systems is nicely illustrated by the values of the energy transfer rate parameter over the region of the similar values of the diffusion coefficients among the different types of the systems. The efficient energy transfer resulting in higher values of the overall energy transfer rate parameter in dilute systems, as seen over this region, is attributed to the reduction in the energy migration and the solvent excimer formation processes which compete efficiently with the final solvent-solute energy transfer process. And
though dilution causes a decrease in the energy migration coefficient, this decrease is offset by a consequent increase in the effective transfer distance.

Thus our results provide lucid and concrete empirical evidences to the facts which hitherto were, perhaps, largely speculative. Nevertheless, these studies have further led to many interesting problems that have still to be explored in the light of the present results.

Since the presence of neutral molecules in the scintillator systems inhibits energy migration and enhances the solvent-solute energy transfer process resulting in the decrease of the energy migration coefficient and increase of the effective transfer distance, experiments at various degrees of dilution of the scintillator systems as a function of temperature would help to know more about the energy migration coefficient, the effective transfer distance and any probable correlation in the behaviour of these two parameters. It would be worthwhile to investigate independently the systems involving a scintillator solvent which forms excimers and the other does not and compare the results of these different types of the systems. This might give a fresh insight into the nature of the energy migration as well as the transfer process. Moreover as the energy migration coefficient and the effective transfer
distance are the variable parameters which depend on the molecular environments, experiments involving a few scintillator systems over a limited range of dilution, viscosity, temperature may sometimes quite fortuitously, lead to erroneous conclusions in favour of either one or the other hypothesis. It is hence necessary to investigate quite a number of scintillator systems involving molecules widely differing in size, structure, spectral characteristics and the Forster critical transfer distance many times the molecular diameter over a wide range of dilution, viscosity and temperature. These studies would then lead us to more meaningful generalizations.

Also, as major changes in the energy transfer process occur due to changes in the fluorescence lifetime of the transferring solvent, determination of the solvent fluorescence lifetime is much useful for the study of the energy transfer process. And as is evidenced by the present investigation that there exist, in some cases, discrepancies between the microviscosity and the macroviscosity of the solvent medium, it is essential that these studies should comprise of the measurement of diffusion coefficients of the scintillator molecules for a precise understanding of the energy transfer phenomenon.
Quenching studies of energy transfer at various degrees of dilution of the scintillator systems and at different temperatures may also provide rich information to probe into the nature of the energy transfer process. Such quenching studies, in this laboratory, are currently in progress.

We hope, some of these studies on the proposed lines in this thesis would help in future to know more regarding the mechanism of energy transfer process between organic molecules - the primordial building blocks of all the living matter.