

## An unique method of determining the excitation energy migration coefficient in organic liquid scintillators

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**Abstract.** An experimental method is described to determine the excitation energy migration coefficient  $\Lambda$  in an organic liquid scintillator by measuring the energy transfer rate parameter  $k_3$  and the quenching rate parameter  $k_{7b}$  as a function of temperature in the range of 20°C–70°C. In this experiment we have used toluene as donor, ethyl-1-*n*-butyl-2-methyl-5-hydroxyindole-3-carboxylate (EBMHC) as acceptor and bromobenzene as quencher. The values of  $\Lambda$  are found to be in good agreement with literature values. Hence this method can be used to determine the migration coefficient in organic liquid scintillators.

**Keywords.** Energy transfer; quenching; scintillators.

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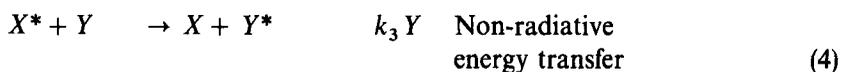
### 1. Introduction

It is well-known that in solids the transfer of excitation energy from excited donor molecule to unexcited acceptor molecule is due to the migration of excitation energy through the medium (Kao and Hwang 1981; Lumb 1978; Turro 1978; Powell and Soos 1975; Birks 1970) in which the excitation energy migrates from one donor molecule to another donor molecule and finally gets transferred to the acceptor molecule. On the other hand in the case of liquids the transfer of singlet excitation energy from donor (solvent) molecules to acceptor (solute) molecules is influenced by long-range donor-acceptor energy transfer as well as the Brownian diffusion of the interacting molecules. The electronic excitation energy migration coefficient  $\Lambda$ , like the mass diffusion coefficient, is a basic physical quantity and although there exist many methods of measuring the excitation energy migration coefficient in solids (Kao and Hwang 1981) there has not been so far (Sipp and Voltz 1983; Morrison and Pandey 1983) a method of determining experimentally  $\Lambda$  in liquids.

In the present investigation we describe an experimental method to determine  $\Lambda$  in the donor-acceptor energy transfer and donor-quencher energy transfer with ethyl-1-*n*-butyl-2-methyl-5-hydroxyindole-3 carboxylate (EBMHC), as acceptor. The results of various parameters determined in the experiment are reported for the acceptor in deoxygenated toluene (donor) using bromobenzene (quencher) as an external quencher under ultraviolet excitation in the 20°C–70°C temperature range.

## 2. Theory

When the ultra-violet radiation of proper wavelength is used to excite the donor, the donor molecules get excited to a particular excitation level and transfer part of their excitation energy to the acceptor molecules which fluoresce. Depending upon the nature of the donor, acceptor and quencher, the quencher molecule may quench either the excited donor molecule or the excited acceptor molecule or both. The phenomenon of energy transfer and quenching in liquid scintillators can be explained by the following kinetic scheme in which  $X$  and  $Y$  represent the donor and the acceptor molecules and an asterisk represents the excited state of the molecule, and  $k$  the corresponding rate parameters.



During the external quenching, which quenches only the solvent, the following reaction may occur



Here  $Q_b$  represents the molecular species of the quencher as well as its concentration. The fluorescence intensity  $I$  in the presence of an external quencher of concentration  $Q_b$  is given by

$$I = \frac{k_0 k_3 Y}{k_1 + k_2 X + k_3 Y + k_{7b} Q_b k_3 Y + k_5 + k_6} \quad (9)$$

If  $I_0$  is the fluorescence intensity in the absence of the external quencher, then the ratio  $I_0/I$  is given by the Stern-volmer equation,

$$I_0/I = (1 + \gamma Q_b) \quad (10)$$

where

$$\gamma^{-1} = \frac{(k_1 + k_2 X)}{k_{7b} Q_b} + \frac{k_3 Y}{k_{7b} Q_b} \quad (11)$$

Thus if one measures  $I$  as a function of  $Q_b$  one can determine from (10) the quenching constant  $\gamma$  at a fixed solute concentration  $Y$ . Further from (11) a plot of  $\gamma^{-1}$  against  $Y$  is a straight line with the intercept

$$i = (k_1 + k_2 X)/k_{7b} Q_b$$

and slope

$$s = k_3/k_{7b}. \quad (13)$$

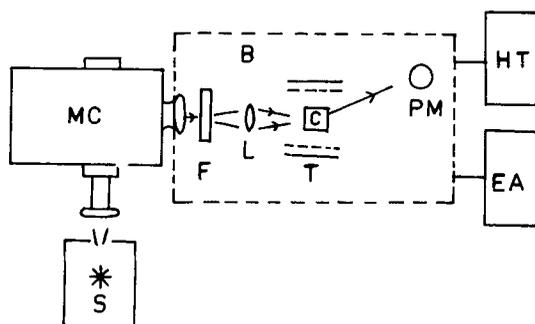
Using the literature value of  $(k_1 + k_2X)^{-1}$  which is the decay time  $\tau_x$  of the donor in the absence of the acceptor one can determine  $k_3$  and  $k_{7b}$  from (12) and (13) respectively at each temperature.

### 3. Experimental details

The experimental arrangement is shown in figure 1. Ultra-violet radiation from a 400 W mercury lamp (S) was dispersed in a Beckman DK-2A spectrophotometer (MC) and the radiation of selected wavelength namely 265 nm line of mercury which corresponds to the first excited state of the donor toluene was focussed using a quartz lens (L) on to a quartz cell (C), containing the solution. The cell was placed in the Beckman temperature controlling unit (H). A narrow band filter (F) was put at the slit of the monochromator to avoid any stray radiation entering the solution. An RCA IP28 photomultiplier (PM) placed slightly off the direction of the incident radiation was used to detect the fluorescence intensity and the photomultiplier output current was measured using a ECIL electrometer amplifier. The temperature controlling unit and the photomultiplier assembly were housed in a black light proof box to protect the photomultiplier from outside light.

The same quantity of solution at different quencher concentrations (0.02, 0.04, 0.06, 0.08 and 0.1 M/l) and at a fixed acceptor concentration was taken in a rectangular quartz cell having an air tight stopper. This procedure was repeated for all the acceptor concentrations (0.5, 0.8, 1.0, 2.0 and 3.0 g/l). The solution was deoxygenated by bubbling dry nitrogen into the cell under nitrogen atmosphere to remove all the oxygen dissolved in the solution. The cell was closed under nitrogen atmosphere to ensure that the solution is free from oxygen. The cell was then placed into the cell holder of the Beckman temperature controlling unit.

First the fluorescence intensity  $I_0$  was measured without the quencher and then the fluorescence intensity  $I$  was measured at different quencher concentrations at a fixed acceptor concentration  $Y$  at each temperature. The error in the measurement



**Figure 1.** A schematic sketch of the experimental arrangement. S: uv source, MC: monochromator, F: narrow band optical filter, L: quartz lens, C: suprasil cell, T: Beckman temperature regulated cell holder, PM: photomultiplier, B: light proof box, HT: negative d-c power supply, EA: electrometer amplifier.

of these values is within 5%. The Stern-Volmer plots,  $I_0/I$  against the quencher concentration  $Q_b$  for different acceptor concentrations at each temperature are found to be linear. According to these plots the intercept should be equal to unity and the slope should be equal to the quenching constant  $\gamma$ . It was found that the intercepts are almost unity and the small deviations may be due to the experimental error.

#### 4. Results and discussion

In figure 2 we give the plots of  $\gamma^{-1}$  against the acceptor concentration  $Y$  at each temperature. The least square fit values of the intercept  $i = (k_1 + k_2 X)/k_{7b}$  and the slope  $s = k_3/k_{7b}$  are determined at each temperature. As explained earlier we have calculated  $k_3$  and  $k_{7b}$  by using these least square fit values of the intercepts and slopes. Here  $(k_1 + k_2 X)^{-1}$  is the decay time  $\tau_x$  at a given temperature  $T$ . We have used the values of  $\tau_x$  determined by (Levin *et al* 1968). Wherever necessary we have used the interpolated values of  $\tau_x$  at temperature relevant to our experiment. These values of  $\tau_x$  are given in table 1 along with the values of  $k_3$  and  $k_{7b}$ .

In order to interpret  $k_3$  and  $k_{7b}$  it is necessary to know the values of the diffusion coefficients  $D_x$ ,  $D_Y$  and  $D_Q$  of the donor, acceptor and quencher molecules respectively. We have determined the values of the diffusion coefficients at the respective temperatures as explained below.

We have used experimentally measured (Mathad *et al* 1985) values of viscosity at various temperatures using a standard Ostwald viscometer and a temperature regulated waterbath whose temperature could be controlled within an accuracy of  $\pm 0.01^\circ\text{C}$ . The values of the viscosities were reproducible within an error of 5%. Further, using the Stokes-Einstein relation,

$$D = kT/a\pi\eta R \quad (14)$$

where  $k$  is the Boltzmann constant,  $T$  the absolute temperature,  $\eta$  the viscosity of the medium,  $R$  the radius of the molecules and  $a$  is the Stokes-Einstein number. The radii of the molecules are calculated by adding the atomic volumes of all the atoms constituting the molecule as suggested by Edward (1956). It is known that (Tyrrell 1961; Sutherland 1905; Mathad *et al* 1986; Umarjee 1985) for self diffusion  $a = 3$  and for diffusion of larger molecules in a liquid of smaller molecules  $a = 6$ . In fact Mathad *et al* (1986) have observed that the experimentally determined values of  $D$  agree with the calculated values with  $a = 3$  for slip condition and  $a = 6$  for stick condition in (14). In our case since the radius of the acceptor molecule is larger than those of the donor and the quencher molecules, the value of  $a$  is taken to be 6 for the acceptor and 3 for the donor and quencher molecules. The values of the diffusion coefficients  $D_x$ ,  $D_Y$  and  $D_Q$  for the donor, acceptor and quencher molecules are calculated according to (14) at different temperatures and are given in table 1.

Now we use the compact equation (Umarjee and Chikkur 1985) which combines both Voltz *et al* and Birks and Conte model and it is given by,

$$\begin{aligned} k_3 \text{ or } k_{7b} &= 4\pi N(D + \Lambda)PR_{\text{eff}} \\ &= 4\pi NDPR_{\text{eff}} + 4\pi N\Lambda PR_{\text{eff}} \end{aligned} \quad (15)$$

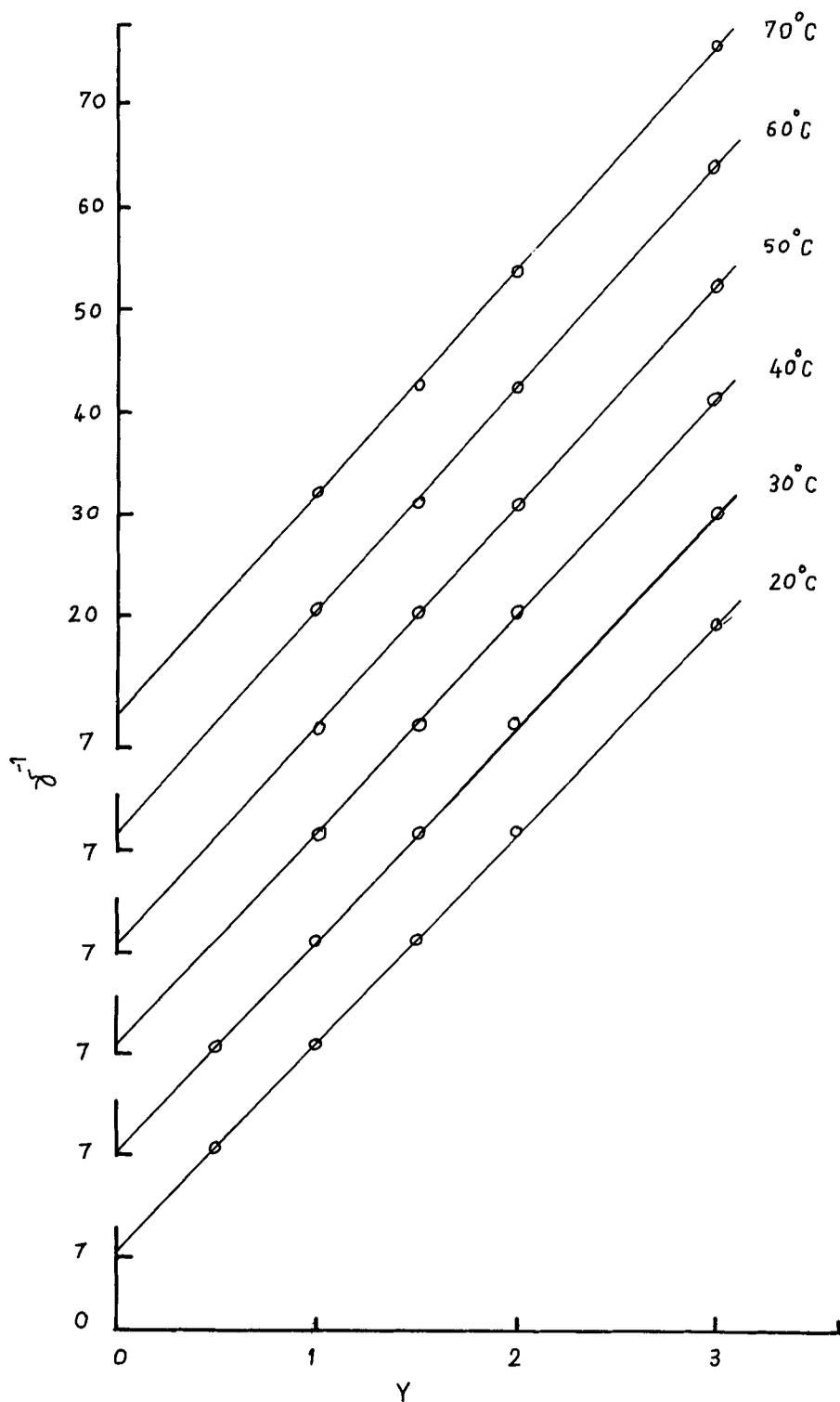


Figure 2. Variation of  $\gamma^{-1}$  (in L/M) with acceptor concentration  $Y$  (in g/L) in the 20–70°C temperature range.

**Table 1.** The values of  $\tau_x$  (in  $10^{-9}$  s), the energy transfer rate parameter  $k_3$  (in  $10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ) and the quenching rate parameter  $k_{7b}$  (in  $10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ) the diffusion coefficients ( $D_x$ ) of donor ( $D_Y$ ) of acceptor and ( $D_Q$ ) of quencher in toluene (in  $10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ) at temperature  $t$ , the values of the migration coefficients  $\Lambda k_3$  and  $\Lambda k_{7b}$  (in  $10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ).

$t^\circ\text{C}$	$\tau_x$	$k_3$	$k_{7b}$	$D_x$	$D_Y$	$D_Q$
20	19.0	5.08	1.07	2.44	0.88	2.39
30	18.2	5.65	1.21	2.83	1.03	2.77
40	17.0	6.26	1.33	3.30	1.20	3.24
50	15.7	6.50	1.36	3.76	1.36	3.68
60	14.5	6.88	1.50	4.30	1.56	4.21
70	13.2	7.18	1.55	4.96	1.80	4.85

$R_x = 2.88 \text{ \AA}$      $R_Y = 3.97 \text{ \AA}$      $R_Q = 2.94 \text{ \AA}$   
 $k_3 = 5.62 \pm 0.667$      $k_{7b} = 7.078 \pm 0.0805$   
 $P_{XY}R_{\text{eff}} = (7.86 \pm 0.93) \text{ \AA}$      $P_{XQ}R_{\text{eff}} = (1.24 \pm 0.14) \text{ \AA}$

where,

$$R_{\text{eff}} = R_0/2 \quad (\text{Voltz } et \text{ al (1966) model})$$

$$= R_{XY} \quad (\text{Birks and Conte model})$$

and

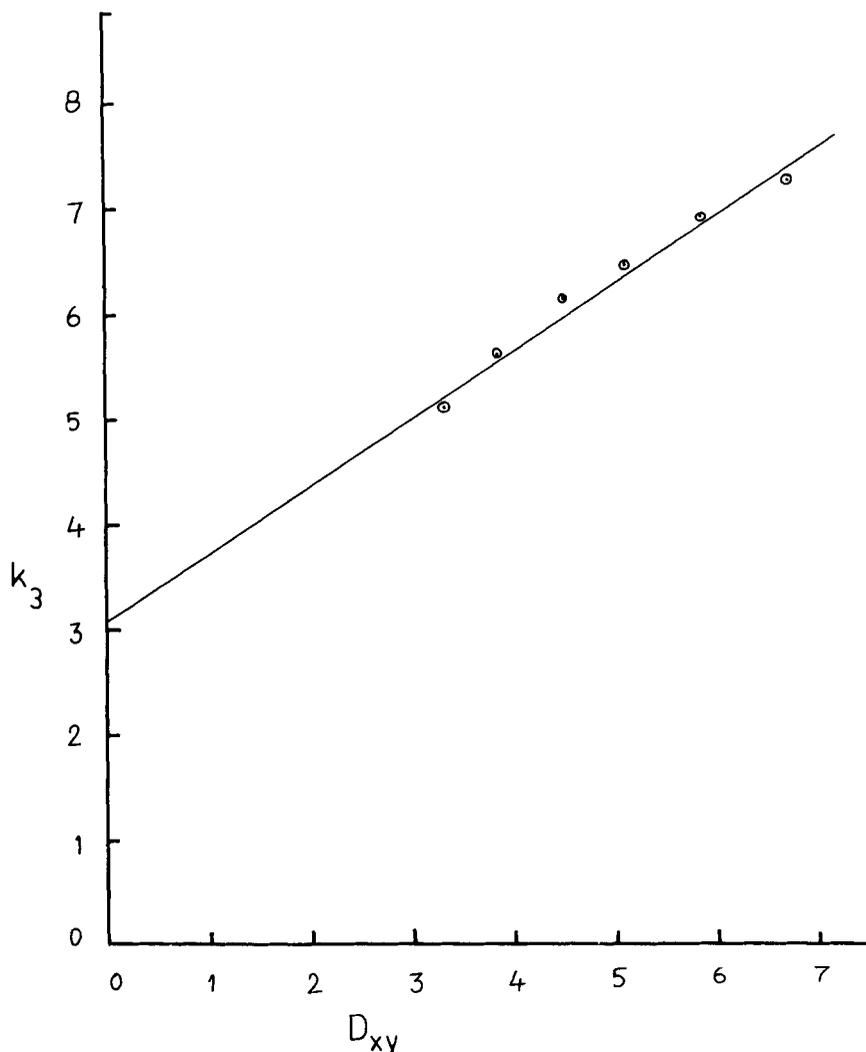
$$D = D_{XY} = (D_X + D_Y), \quad P = P_{XY} \text{ for } k_3$$

$$D = D_{XQ} = (D_X + D_Q), \quad P = P_{XQ} \text{ for } k_{7b}$$

$P$ , the probability of energy transfer per encounter,  $R_0$  the Forster critical energy transfer distance (Forster 1948),  $P_{XY}$  the probability of energy transfer per encounter between the donor and acceptor molecules, which is always unity,  $P_{XQ}$  the probability of quenching per encounter between the donor and the quencher molecules which is always less than unity, and is used to determine  $\Lambda$  from (15), we have used the experimentally determined values of  $k_3$  and  $D_{XY}$  and  $k_{7b}$  and  $D_{XQ}$ .

In figure 3 we display the plots of  $k_3$  against  $D_{XY}$  in figure 4 the plots of  $k_{7b}$  against  $D_{XQ}$  according to (15). The solid lines correspond to the least square fit straight lines and the points are the experimental values. The least square fit values of  $\Lambda k_3$  and  $P_{XY}R_{\text{eff}}$  corresponding to  $k_3$  and  $\Lambda k_{7b}$  and  $P_{XQ}R_{\text{eff}}$  corresponding to  $k_{7b}$  are calculated by taking the ratio of intercept to slope of the straight lines in each case and the values are given in table 1. The fact that the experimental values of  $k_3$  and  $D_{XY}$ ,  $k_{7b}$  and  $D_{XQ}$  follow (15) shows that  $\Lambda$  is independent of temperature. Further from the values of  $\Lambda k_3 = (5.62 \pm 0.667) 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  and  $\Lambda k_{7b} = (7.078 \pm 0.0805) 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ , we see that they differ by about 20% from their mean value of  $\Lambda = (6.349 \pm 0.3738) 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  provided we take the extreme values of  $\Lambda$  in both the cases. Even then the mean value of  $\Lambda$  determined by us lies well within the range of  $\Lambda$  ( $3 - 10 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ) determined by others (Birks 1970; Birks and Conte 1968; Mathad *et al* 1986) for toluene. This unequivocally proves that  $\Lambda$  is an intrinsic property of a given liquid.

Further we see from table 1 that the value of  $R_{\text{eff}} = (7.86 \pm 0.93) \text{ \AA}$  assuming  $P_{XY}$  to be unity, since according to Birks and Conte model the probability of energy transfer  $P_{XY}$  is taken to be unity always. The average of the two extreme values i.e.,  $(7.86 + 0.93) \text{ \AA}$  and  $(7.86 - 0.93) \text{ \AA}$  of  $R_{\text{eff}}$  equal to  $7.86 \text{ \AA}$  is about 13% larger than  $R_{XY} = (R_X + R_Y)$  the sum of the molecular radii of the two interacting molecules viz. donor and acceptor

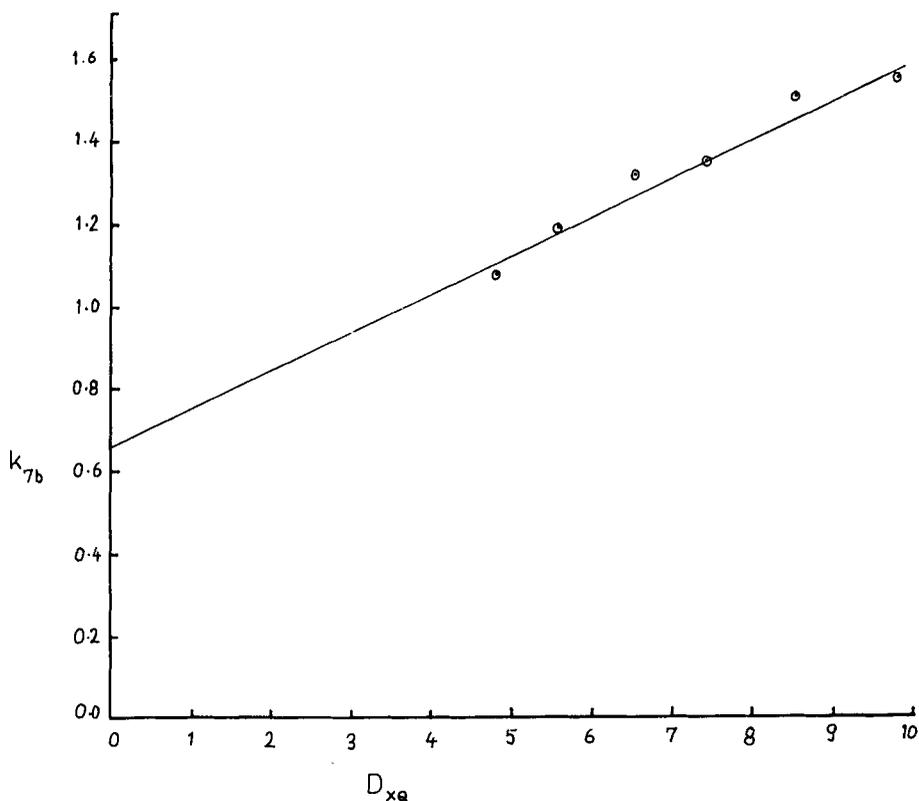


**Figure 3.** Variation of  $k_3$  (in  $10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ) with  $D_{XY}$  the sum of the self-diffusion coefficients of the donor and the acceptor (in  $10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ).

equal to  $6.85 \text{ \AA}$  calculated independently using the method suggested by Edward. On the other hand the average value of  $R_{\text{eff}} = 7.86 \text{ \AA}$  is about 18% smaller than  $R_0/2 = 9.3 \text{ \AA}$  calculated using Forster equation (Forster 1948). This shows that  $R_{\text{eff}}$  is close to  $R_{XY}$ .

From table 1 we see that the value of  $P_{XQ}R_{\text{eff}} = (1.24 + 0.14) \text{ \AA}$  is much smaller than  $R_{XQ} = 5.82 \text{ \AA} = (R_X + R_Q)$ . According to Birks and Conte model (1968) the probability of quenching per encounter may be less than unity. Hence if we take  $P_{XQ}$  to be  $0.213 \pm 0.024$  the value of  $R_{\text{eff}}$  agrees with that of  $R_{XQ}$ . The fact that  $R_{\text{eff}} = R_{XY}$  in the case of energy transfer and  $R_{\text{eff}} = R_{XQ}$  in the case of quenching shows that Birks and Conte model holds good for energy transfer as well as quenching which evidently shows that both energy transfer and quenching processes are due to close collision between the interacting molecules.

The mean value of  $\Lambda$  obtained in the present study is equal to  $(6.349 \pm 0.3738)$ .



**Figure 4.** Variation of  $k_{7b}$  (in  $10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ) with  $D_{xq}$  the sum of the self-diffusion coefficients of the donor and the quencher (in  $10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ).

$10^{-5} \text{ cm}^2 \text{ s}^{-1}$ . Birks and Conte (1968) estimated it to be  $7.5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  assuming  $R_{\text{eff}}$  to  $R_x + R_y$ , Tanielian estimated  $\Lambda$  to be  $5.5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  from quenching studies where the final step is generally accepted to be collisional. On the other hand Voltz *et al* estimated  $\Lambda$  to be  $4.0 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  assuming  $R_{\text{eff}}$  to be  $R_0/2$ . Estimated values of  $\Lambda$  reported by others (Birks 1970; Sutherland 1905) lie in the range of (3 to  $10 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ). But their values depend on what they assume for the final step of energy transfer. The fact that our mean value of  $\Lambda$  lies within the values estimated by Birks and Conte (1968) and Tanielian (1965) assuming the final step of energy transfer as due to close collision supports our conclusion arrived at for the final step of energy transfer on the basis of the values of  $R_{\text{eff}}$  as due to close collision. However, we find that there is a large variation in the values of  $\Lambda$  estimated on the basis of the assumptions made for the final step of energy transfer. This may be due to the fact that the exact determination of  $R$  itself is not unique in liquids.

Hence we may say that the present method of estimating the energy migration coefficient in liquids offers an unique way since it does not depend upon  $R$ .

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