Comments on the Mean Diffusion Length of Luminescent Molecules in Solutions *

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The effect of concentration of donor and acceptor molecules on the mean diffusion length in solutions is discussed.

The influence of mass diffusion on the nonradiative electronic excitation energy transfer (NEEET) in luminescent solutions has been the subject of numerous publications [1–3].

In the discussion of this problem several zones have been distinguished limited by the critical distance R_{0A} for the NEEET from D^* to A and by the mean diffusion length $\bar{r}_0$, defined as [1]

$$\bar{r}_0 = (2\mathscr{D}\,\tau_{0D})^{1/2}. \tag{1}$$

In (1) τ_{0D} is the mean decay time of fluorescence (FL) of the donor D in the presence of the acceptor A, and $\mathscr{D}$ equals $\mathscr{D}_D + \mathscr{D}_A$, where $\mathscr{D}_D$ and $\mathscr{D}_A$ are the diffusion coefficients of D and A, respectively.

It follows from theoretical considerations that mass diffusion should increase the efficiency of NEEET [3, 4]. Results of experimental investigations are ambiguous. Some authors report a considerable influence of diffusion on NEEET [5, 6], while only a slight or even negligible effect has been observed by others [7, 8].

Such discrepancies might have arisen for many reasons [3]. In our opinion, they may also be the result of considering the diffusion length $\bar{r}$ to be a constant independent of the concentration of D and A in the solution.

Relation (4) is regarded as more general than formula (3). Indeed, if monomer quenching is excluded

Values of $\bar{r}_0$ as calculated according to (1) are correct only for $R_{DA} \gg R_{0A}$, where R_{DA} is the mean distance between D^* and A. If, however, this inequality is not satisfied at higher concentrations, then the mean diffusion length $\bar{r}$ can be much shorter than $\bar{r}_0$ due to the additional deactivation channel for D^* molecules by NEEET from D^* to D and A.

For sufficiently high concentrations the time of localization of the excitation energy on a D^* molecule,

$$\tau_1 = \Big(\sum_D k_{D^*D} + \sum_A k_{D^*A} + k_F + k_q\Big)^{-1},$$

can be much shorter than the decay time τ_{0D} (k_{D^*D}, k_{D^*A}, k_F and k_q are the rate constants for NEEET from D^* to D, D^* to A, FL emission and internal conversion, respectively). In such a case the actual diffusion length should be calculated from relation (1) by substitution of τ_{0D} with τ_1, i.e.

$$\bar{r} = (2\mathscr{D}\,\tau_1)^{1/2}. \tag{2}$$

The localization time τ_1 has been determined [9, 10] to be

$$\tau_1 = \tau_{0D}\,\frac{1+\gamma^2-(1.5+\gamma^2)f}{1-f}; \tag{3}$$

$$\gamma = \tfrac{1}{2}\pi^{1/2}(C_D/C_{0A} + C_A/C_{0A}) = \gamma_D + \gamma_A,$$

$$f \equiv f(\gamma) = \pi^{1/2}\,\gamma\,\exp(\gamma^2)\,[1-\operatorname{erf}(\gamma)].$$

Recently a more exact relation has been derived [11]:

$$\tau_1 = \tau_{0D}\,\varphi(\gamma,\alpha,\alpha_0) \tag{4}$$

where

$$\varphi(\gamma,\alpha,\alpha_0) = \frac{1+\gamma^2-(1.5+\gamma^2)f+\alpha_0\alpha f(f+\gamma^2-0.5)-\alpha_0\alpha\gamma^2}{1-f}\,;\ \alpha = \gamma_D/\gamma\,. \tag{5}$$

α_0 is the probability of the excitation energy not being degraded during its transfer between donor molecules.

($\alpha_0 = 1$) then for $\gamma_A \gg \gamma_D$, $\alpha \to 0$ and relation (4) becomes identical with (3). For $\gamma_D \gg \gamma_A$ relation (4) has a particularly simple form

$$\tau_1 = \tau_{0D}(1-f)\,. \tag{6}$$

Substitution of (4) into (2) leads to

$$\bar{r} = \bar{r}_0[\varphi(\gamma,\alpha,\alpha_0)]^{1/2}. \tag{7}$$

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Figure 1 shows changes of $\bar{r}$ as dependent on the reduced concentration γ for several values of α. Curves 1 and 3 correspond to the limiting values $\alpha = 0$ and $\alpha = 1$. Curve 2 was calculated for $\gamma_D = \gamma_A$, $(\alpha = 1/2)$. Comparison of curves 1 and 3 shows that large variations of the ratio γ_D/γ_A have a relatively small effect on the concentration dependence of τ_1, and thus $\bar{r}$. It is evident from the figure that the actual diffusion length $\bar{r}$ can for high concentrations be much smaller than $\bar{r}_0$. For $\gamma = 1$, $(C_A \approx C_{0A})$, $\bar{r}$ is already equal to approximately $\bar{r}_0/2$, while for $\gamma = 10$, $\bar{r}$ drops by more than one order of magnitude (see curve 1). It is thus possible that the discussion based on the value $\bar{r}_0$ instead of r can lead in some cases to the erroneous conclusion that mass diffusion does not affect the NEEET process in solutions.

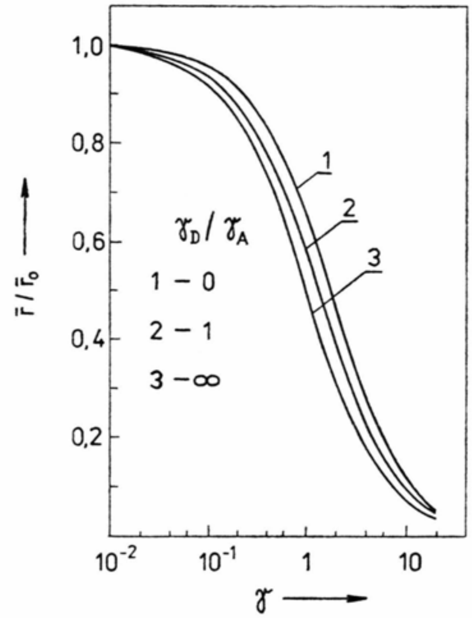

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Fig. 1. Actual diffusion length $\bar{r}$ vs reduced concentration for different values of γ_D/γ_A and $\alpha_0 = 1$, calculated from (7).

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