Diffusion-Limited Energy Transfer from Dy^{3+} to Ho^{3+} in Dimethyl Sulfoxide

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Diffusion-limited energy transfer has been studied from Dy^{3+} to Ho^{3+} in dimethyl sulfoxide. The value of the diffusion constant has been calculated to be 4.65×10^{-14} cm² sec⁻¹ at 300 K. A temperature-dependent study of energy transfer has also been carried out. The probabilities of energy transfer P_{da} and transfer efficiency η_T have been calculated. © 1987 Academic Press, Inc.

Introduction

The theory of nonradiative energy transfer from one ion (donor) to another ion (acceptor) has been discussed by several authors. Considerable work has been done so far on energy-transfer processes in glasses (*1–6*) and in solutions (*7–14*), under different conditions, in studying the mechanism of energy transfer that takes place during the quenching of excited rare-earth ions by ion–ligand interaction, ion–ligand–ion interaction, or ion–ion interaction, etc. Preliminary approaches to finding the mechanism of energy transfer were taken by Forster (*15*) and Dexter (*16*) and later by Inokuti and Hirayama (*17*). The problem was treated further by Yokota and Tanimoto (*18*), taking diffusion of excitation energy into account.

When a system containing randomly distributed donors and acceptors, where migration of excitation energy among donors is absent, is optically excited, the decay of the donor emission (*17*) as a function of time is given by

$$\phi(t) = \phi(0)\exp\left\{ -\frac{t}{\tau_0} - \frac{C_a}{C_o}\Gamma(1 - 3/S)(t/\tau_0)^{3/S}\right\}. \quad (1)$$

Here τ_0 is the donor decay time; S is the interaction parameter, which is equal to 6 for the dipole–dipole and 8 for the dipole–quadrupole interaction; C_a is the acceptor concentration; and R_0 is the critical transfer distance corresponding to the critical concentration C_o ($C_o = 3/4\pi R_0^3$), for which the probabilities of transfer and emission of the excited donor are equal.

At low acceptor concentrations migration of excitation energy among donors is more favorable and the observed values of decay of donor emission, $\phi(t)$, can be expressed (*18*) by using the relation

$$\phi(t) = \phi(0)\exp\left\{ -\frac{t}{\tau_0} - \frac{4}{3}\pi^{3/2}C_a\left(R_0^6\frac{t}{\tau_0}\right)^{1/2} \left(\frac{1 + 10.87x + 15.5x^2}{1 + 80.743x}\right)^{3/4}\right\}. \quad (2)$$

where $x = D_d C_o^{-1/2}t^{2/3}$ (D_d is the diffusion

constant). Relation (2) is followed by a dipole–dipole interaction mechanism of energy transfer from donor to acceptor. Diffusion increases the transfer efficiency. The study of time-dependent decay of the donor Dy^{3+} following flash excitation has enabled us to examine the transfer mechanism from Dy^{3+} to Ho^{3+} in dimethyl sulfoxide (DMSO).

Experimental Procedure

Dy$_2$O$_3$ and Ho$_2$O$_3$ (99.9% Indian Rare Earths, Kerala, India) were converted to chlorides by treatment with hydrochloric acid (spectrograde) and by crystallization from concentrated solutions. The anhydrous chlorides were dissolved in dimethyl sulfoxide (Riedel, Germany). The samples were vacuum sealed immediately and were kept in a cool, dry place. The fluorescence spectra and decay times were taken at 80, 300, and 333 K in the usual manner.

Results and Discussion

The luminescence characteristics of rare-earth ions in organic solvents depend strongly upon solvent molecules and it has been found that the fluorescence yield is relatively low in many organic solvents because of the presence of high-frequency vibrational modes associated with the solvent under consideration, e.g., due to the presence of O–H, –NH, and C–H vibrational groups. The fluorescence yield of the rare-earth ions also depends, to a considerable extent, upon the solvent molecules in the primary solvation sphere (18–20). It is observed in the present case that the fluorescence yield of Dy^{3+} in dimethyl sulfoxide increases considerably compared to its yield in other organic solvents. The fluorescence spectra of Dy^{3+} (0.5 M) in DMSO and other organic solvents at 80, 300, and 333 K have been reported elsewhere (21). Light excitation of Dy^{3+} ion in DMSO is

accompanied by fluorescence emission, which always originates from the lowest excited state of Dy^{3+}, viz., the $^4F_{9/2}$ state. Regardless of the exciting wavelength, there is no transfer of energy from solvent to solute molecules. It is observed that the fluorescence yield increases twofold at 80 K. However, at 333 K it becomes half of the yield at 300 K. The observed transitions are $^4F_{9/2} \rightarrow {}^6H_{13/2}$ (570 nm) and $^4F_{9/2} \rightarrow {}^6H_{15/2}$ (480 nm). The observed decay times which are exponential in nature for the $^4F_{9/2}$ state are 1.1, 0.7, and 0.4 msec at 80, 300, and 333 K, respectively. The absorption peaks of Ho^{3+} lie at 445 and 570 nm. There is an overlap of strong absorption of Ho^{3+} and strong emission of Dy^{3+} ions in DMSO, and the emission intensity diminishes very rapidly, indicating a transfer of energy from Dy^{3+} to Ho^{3+}. The fluorescence spectrum of Dy^{3+} at 300 K corrected for the absorption spectrum of Ho^{3+} in the presence of Ho^{3+} is shown in Fig. 1. The selective dips observed in the $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition indicate the presence of a radiative energy transfer from Dy^{3+} to Ho^{3+}. The emission intensity of the transition $^4F_{9/2} \rightarrow {}^6H_{13/2}$ also reduces considerably though there is no overlap of this transition with any absorption band of Ho^{3+}. Weak visible fluorescence of Ho^{3+} has been observed in phosphate glasses arising from the $^5S_2$, $^5F_4$, and $^5F_5$ to the termination $^5I_8$ level. The intensity of this fluorescence increases considerably in tellurite glasses because of smaller multiphonon relaxation (22). In the present study, no such fluorescence has been observed, which may be due to the presence of high-frequency vibrational modes of DMSO. The other emissions would be in the infrared region, but they could not be recorded due to experimental limitations. The decay times which are exponential in nature at the aforementioned temperatures, however, reduce in value and change to nonexponential nature, showing a nonradiative energy transfer from Dy^{3+} to Ho^{3+} in DMSO.
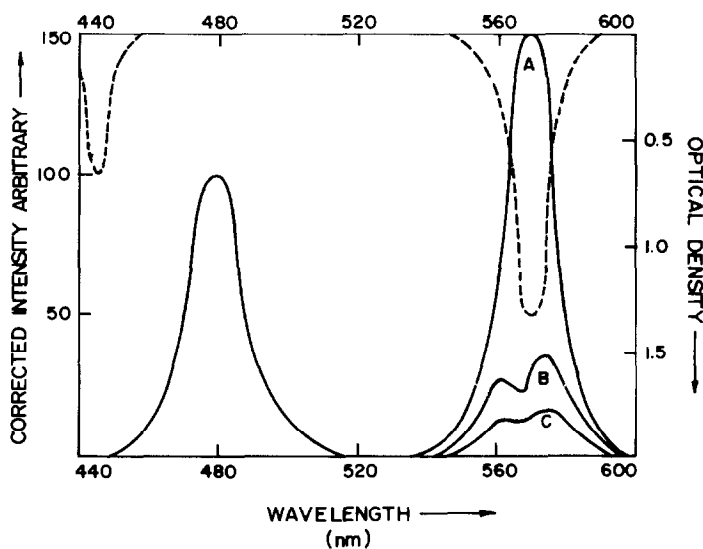
FIG. 1. Emission spectra at 300 K. (A) Dy^{3+} (0.5 M); (B) Dy^{3+} (0.5 M) + Ho^{3+} (1.5 M); (C) Dy^{3+} (0.5 M) + Ho^{3+} (2 M). The dotted curve shows the absorption spectrum of Ho^{3+}.

To examine whether the energy transfer is a dipole–dipole, a dipole–quadrupole, or a quadrupole–quadrupole interaction (when the acceptor concentration is higher than that of the donor) the observed values of $\phi(t)$ are compared with the calculated values of $\phi(t)$. The observed and calculated values of $\phi(t)$ agree within experimental error for interaction parameter, S equal to 6, suggesting a dipole–dipole interaction mechanism of energy transfer at the above temperatures. The decay curves of Dy^{3+} taken at 80, 300, and 333 K in the absence and presence of Ho^{3+} are shown in Figs. 2a–c. The solid lines represent the experimental curves and the black circles the values of $\phi(t)$ calculated from Eq. (1), keeping $S = 6$.

To confirm the transfer mechanism we proceed as follows. The fluorescence intensity of the donor emission (23) follows the relation

$$\frac{I}{I_0} = \frac{\tau}{\tau_0} = \{1 + \beta(C_a/C_o)^{\theta/3}\}^{-1}, \quad (3)$$

where τ and τ_0 are the decay times and I and I_0 are the emission intensities of the donor in the presence and absence of acceptor ions, respectively, and β is a constant. Equation (3) can be written

$$\log[(I_0 - I)/I] = \log \beta + \frac{\theta}{3} \log(C_a/C_o). \quad (4)$$

The straight lines obtained by plotting $\log[(I_0 - I)/I]$ against $\log C_a$ give a value of $\theta = 5.8$, which is very close to 6, confirming a dipole–dipole interaction mechanism. The values of θ at 80 and 333 K are also close to 6, which reaffirms a dipole–dipole interaction.

Energy-transfer efficiency η_T (24) calculated from the relation

$$\eta_T = 1 - I/I_0 = 1 - \tau/\tau_0 \quad (5)$$

at three different temperatures is given in Table I. The figures suggest that a very efficient transfer takes place at 333 K and also that the transfer mechanism is predominantly dipole–dipole in nature.

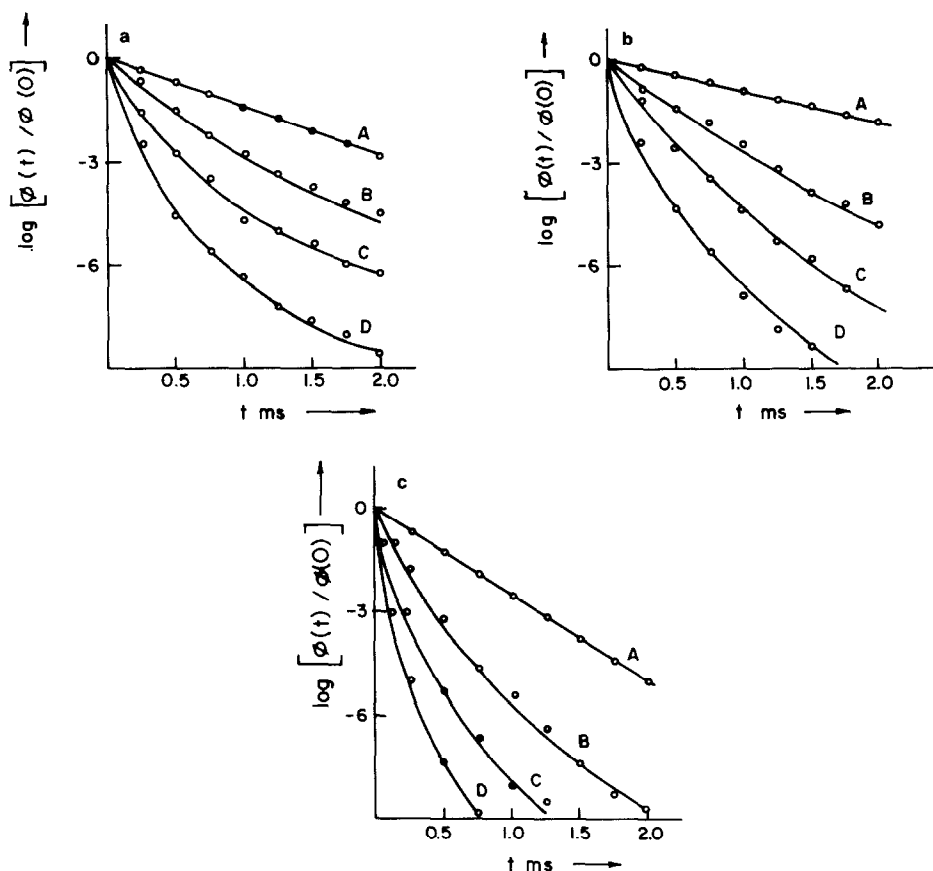P_{da}, the probability of energy transfer (24), is determined using the relation

FIG. 2. Decay curves at 80, 300, and 333 K. (A) Dy^{3+} (0.5 M); (B) Dy^{3+} (0.5 M) + Ho^{3+} (1.5 M); (C) Dy^{3+} (0.5 M) + Ho^{3+} (2.0 M); (D) Dy^{3+} (0.5 M) + Ho^{3+} (2.5 M).

$$P_{da} = \frac{1}{\tau_0}\left(\frac{I_0}{I} - 1\right) = \frac{1}{\tau} - \frac{1}{\tau_0}. \qquad (6)$$

The linear dependence of P_{da} on C_a^2 and also on C^2 (C being the sum of donor and acceptor concentrations) suggest a dipole–dipole interaction mechanism which is consistent with Fong and Diestler's theory (25) that one donor ion interacts with two acceptor ions. The calculated values of P_{da} at 80, 300, and 333 K are presented in Table II and the linear dependence of P_{da} on C_a^2 is shown in Fig. 3. The processes that affect the donor lifetime in a sensitized rare-earth system are (i) intrinsic donor radiative and nonradiative relaxation, (ii) direct relaxa-

TABLE I

ENERGY TRANSFER EFFICIENCY (η_T) FOR THE Dy³⁺ TO Ho³⁺ SYSTEM (CONCENTRATION OF Dy³⁺ FIXED 0.5 M)

Acceptor Ho³⁺ concentration (M)	η_T		
	80 K	300 K	333 K
0.1	0.01	0.02	0.05
0.2	0.02	0.04	0.09
0.5	0.12	0.20	0.25
1.0	0.32	0.36	0.40
1.5	0.40	0.45	0.49
2.0	0.46	0.51	0.56
2.5	0.50	0.56	0.61
3.0	0.63	0.78	0.82

TABLE II

PROBABILITY OF ENERGY TRANSFER (P_{da})
FROM Dy^{3+} TO Ho^{3+} (CONCENTRATION OF Dy^{3+}
FIXED 0.5 M)

Acceptor Ho^{3+} concentration (M)	P_{da}		
	80 K	300 K	333 K
0.1	8.0	24.1	105.2
0.2	14.2	50.0	111.1
0.5	100.0	280.0	370.0
1.0	333.0	625.0	1,333.3
1.5	494.0	1000.0	2,000.0
2.0	550.0	1291.2	2,500.0
2.5	667.0	1700.0	3,333.0
3.0	1110.0	2650.0	18,000.0

tion transfer to acceptors, and (iii) energy migration among donors followed by transfer to acceptor (diffusion-limited relaxation). Process (i) is responsible for the relaxation of the donor when no acceptor is present and when self-quenching is absent. The excited donor decays exponentially. Process (ii) is responsible when the concentration of the acceptor ion is either equal to or greater than that of the donor ion. In such a system a dipole–dipole interaction mechanism is active, as established from experimental observations as well as from theoretical considerations.

The third process occurs at very low acceptor concentrations and is a complicated one. When the concentration of acceptor is very low, a small fraction of Dy^{3+} excited ions are present within the effective interaction sphere of the Ho^{3+} ion. Therefore, the excited donors which lie near the acceptor domain relax predominantly by direct ion–ion interaction but those donors which are at larger distances must diffuse in the vicinity of an acceptor before relaxation occurs. In such a situation the donor decays in a complicated manner. The decay of donor luminescence after pulse excitation behaves in a time-dependent manner, i.e.,

nonexponentially for a short time and exponentially for a longer time, which is a characteristic of the diffusion-limited relaxation mechanism. Diffusion-limited energy transfer between a donor ion and any of the acceptor ions is described by

$$-\frac{\partial \psi_d(\bar{\gamma},t)}{\partial t} = -D_d \nabla^2 \psi_d(\bar{\gamma},t) + \frac{1}{\tau_0} \psi_d(\bar{\gamma},t)$$

$$+ \sum_i V[|\bar{\gamma} - R_{ia}(t)]\psi_d(\bar{\gamma},t), \quad (7)$$

where $\bar{\psi}_d(\gamma,t)$ is the donor distribution wave function, D_d is the diffusion constant, and $\sum_i V[|\bar{\gamma} - R_{ia}(t)]$ is the interaction of a donor with acceptor ions. Yokota and Tanimoto (16) have solved this expression and the solution is expressed in Eq. (2). The diffusion time τ_d and the intrinsic decay time are related by

$$\tau_d^{-1} = \tau_1^{-1} - \tau_0^{-1},$$

where τ_1 is the longer component of the decay time and is obtained by drawing a tangent on the exponential position of the experimentally obtained decay curve. The diffusion constant D_d can be calculated using the relation

$$D_d = (\tau_d 8.5NC_a\alpha^{1/4})^{-4/3}, \quad (8)$$

where α is the coupling constant and is equal to R_0^6/τ_0. Putting R_0 equal to 11.82 Å and τ_0 as 0.7 msec, the value of α is found to be 4.9×10^{-40} cm^6 sec^{-1} from the above and
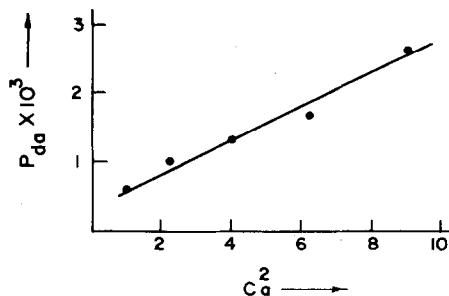

FIG. 3. $P_{da}V_sC_a^2$ curve.

from Eq. (8). The diffusion constant obtained is 4.65×10^{-14} cm^2 sec^{-1}. Diffusion length $d = [(D_d\tau_0)^{1/2}]$, length parameter $l = [0.68(\alpha/D_d)^{1/4}]$, and acceptor-acceptor distances a are 6.45×10^{-8}, 83.95×10^{-8}, and 105×10^{-8} cm, respectively. The criterion for diffusion-limited energy transfer, that $d < l < a$, is very well satisfied in this case, suggesting that the transfer from Dy^{3+} to Ho^{3+} in dimethyl sulfoxide is a diffusion-limited process.

Acknowledgment

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