

ENERGY TRANSFER IN BINARY SOLUTIONS AND ITS ROLE IN DETERMINING THE ABSOLUTE QUANTUM YIELDS AND OTHER RATE PARAMETERS

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(Received May 2, 1978; in revised form July 1, 1978)

Summary

Energy transfer from 1,2,4-trimethylbenzene (donor) to eight other organic molecules (acceptors) in cyclohexane has been investigated at room temperature using a simple kinetic reaction scheme that is independent of both donor and acceptor concentrations. The absolute quantum yields of different acceptors have also been determined very accurately relative to that of the donor. This scheme was found to be independent of donor and acceptor kinetics. Some important rate parameters such as fluorescence and internal quenching rate constants have been evaluated.

1. Introduction

Energy transfer from a donor molecule to an acceptor molecule (of lower energy level than the donor) has been observed by several investigators in liquid [1, 2], solid [3, 4] and plastic [5, 6] scintillators. However, these investigators and others [7] were primarily interested in the efficiency and type of energy transfer that takes place from donor to acceptor molecules. Special efforts were made to differentiate between radiative and non-radiative energy transfer [7] and their nature. Since all these processes are now understood rather well for several scintillator pairs, the technique of energy transfer can be used as a tool in evaluating quantum yields and other impor-

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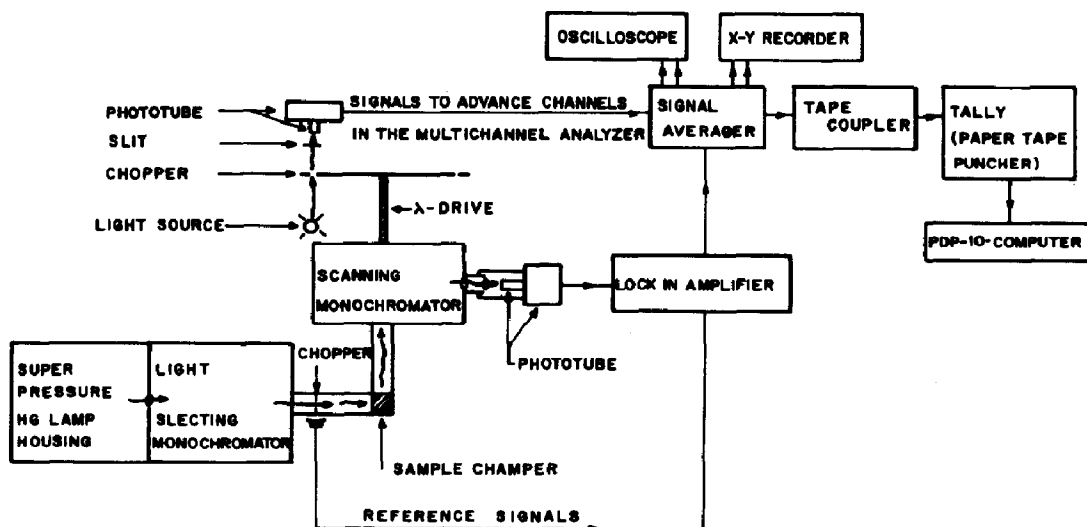


Fig. 1. Block diagram of the experimental arrangement of the fluorescence spectrometer.

tant molecular parameters. The results reported in this paper are an attempt in that direction.

2. Experimental

A block diagram of the experimental set-up used for the measurement of fluorescence emission is shown in Fig. 1. The exciting source is a super-pressure mercury lamp and the light-selecting monochromator is a Bausch and Lomb high intensity grating monochromator ($1200 \text{ grooves mm}^{-1}$). The chopper in front of it is PAR Model 125. The sample container is a rectangular fused quartz cell (10 mm light path) and the sample was excited by a wavelength of 2650 \AA . The scanning monochromator is a 500 mm Bausch and Lomb grating monochromator. The detection and recording system is similar to that discussed in ref. 8. It was found that the combined use of a lock-in amplifier and a signal averager leads to a better signal to noise ratio and also to a much better resolution than the use of either of them separately.

The decay-time experiment is discussed in detail in ref. 9 and the reader should refer to it. A Cary-14 spectrophotometer was used for measurements of the absorption spectra.

All the chemicals used were of spectroscopic quality and were used without further purification. Oxygen was removed from the sample by bubbling high purity dry argon (from Union Carbide Corporation) through the sample for approximately 20 min prior to recording the data. The cell was then sealed and used immediately.

TABLE 1

Values of the fluorescence quantum yields, decay times and other rate parameters for various compounds ^a

Compound	q_A	τ_A (ns)	k_{FA} (ns^{-1})	k_{IA} (ns^{-1})	τ_{FA} (ns)	Percentage of incident radiation absorbed by D (%)
PPO	0.964 ^c , 1.00 [12]	2.0 ^c , 1.4 [12]	0.482 ^c	0.18 ^c	2.075 ^c , 1.44 [12] ^e	> 94 ^d
1-Naphthylamine ^b	0.89 ^c , 0.46 [12]	6.1 ^c , 6.0 [12]	0.146 ^c	0.018 ^c	6.849 ^c , 11.1 [12] ^f	> 99
POPOP	0.90 ^c , 0.93 [12]	2.4 ^c , 1.3 [14]	0.375 ^c	0.042 ^c	2.667 ^c , 1.47 [12]	> 97
	0.86 [14]				1.5 [14]	
1,1'-Binaphthyl	0.70 ^c , 0.77 [12]	3.1 ^c , 3.0 [12]	0.226 ^c	0.097 ^c	4.425 ^c , 3.43 [12] ^e	> 96
Pyrene	0.69 ^c , 0.23 [12]	400.0 ^c , 480.0 [13]	0.0017 ^c	0.0008 ^c	588.24 ^c , 666.7 [16]	> 99
	0.68 [13]	435.0 [17]	0.0015 [16]			
9,10-Dichloranthracene	0.52 ^c , 0.55 [12]	8.8 ^c , 8.5 [12]	0.059 ^c	0.055 ^c	16.89 ^c , 10.2 [12] ^e	> 99
	0.48 [17]	7.2 [17], 9.98 [18]			13.3 ^f , 15.4 [17]	
Naphthalene	0.38 ^c , 0.23 [12]	100.4 ^c , 96.0 [12]	0.0039 ^c	0.006 ^c	256.41 ^c	> 93 ^d
	0.38 [15]					
4-Biphenyl phenyl ether	0.095 ^c , 0.12 [12]	3.0 ^c , 4.8 [12]	0.032 ^c	0.301 ^c	31.25 ^c	> 75 ^d

^aThe values of the D rate parameters are as follows: $q_D = 0.41$ (this work); $\tau_D = 27.5$ ns (this work); $k_{FD} = 0.015$ ns^{-1} (this work); $k_{ID} = 0.021$ ns^{-1} (this work); $\tau_{FD} = 66.7$ (this work) or 74.0 [12].

^bThe value of q_A for this compound has been checked several times and unless our sample was contaminated the value obtained by Beriman [12] is wrong.

^cThis work.

^dCorrection for absorption by A was needed for only one or two of the highest values of C.

^eThe Strickler and Berg [19] formula was used:

$$1/\tau_{FA} = 2.88 \times 10^{-9} n^2 \langle \bar{\nu}^{-3} \rangle_{av}^{-1} \int (\epsilon/\bar{\nu}) d\bar{\nu}$$

where

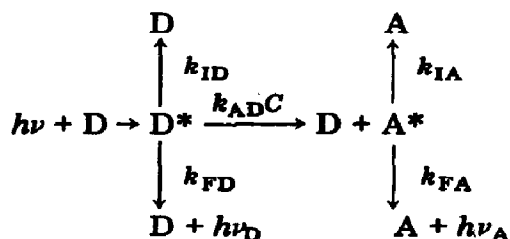
$$\langle \bar{\nu}^{-3} \rangle_{av} = \int \bar{\nu}^3 I(\bar{\nu}) d\bar{\nu} / \int I(\bar{\nu}) d\bar{\nu}$$

^fThe Leushine [20] formula was used:

$$1/\tau_{FA} = 2.88 \times 10^{-9} n^2 \int ((2\nu - \bar{\nu})/\nu) I(\bar{\nu}) d\bar{\nu}$$

3. Results

Energy transfer from a donor molecule D to an acceptor molecule A can be understood using the following kinetic reaction scheme:



where D* and A* are the donor and acceptor molecules respectively in their first π electron singlet states, k_{FD} and k_{ID} are the rate constants for the fluorescence and internal quenching respectively of molecule D, k_{FA} and k_{IA} are the corresponding parameters for molecule A, C is the concentration of A in a solution containing both A and D and K_{ADC} is the rate parameter for the transfer of energy from D* to A. This transfer of energy could be radiative and/or non-radiative [7]. Both donor and acceptor molecules were chosen such that a transfer of energy from A* to D would be impossible. This is because in all cases studied, D has higher energy levels than A [10]. At the exciting wavelength[†] (2650 Å) and at the donor and acceptor concentrations used, the donor alone absorbs nearly all the incident radiation. There was almost no correction for the absorption of incident radiation by the acceptor except at a very few concentrations as indicated in Table 1.

Using the above kinetic reaction scheme, the following equations can be derived (for more details see ref. 8):

$$I_{\text{A}} = q_{\text{A}}KC/(1 + KC) \quad (1)$$

$$I_{\text{D}} = q_{\text{D}}/(1 + KC) \quad (2)$$

where I_{A} and I_{D} are the relative integrated emission intensities of A* and D* respectively;

$$K = k_{\text{AD}}/(k_{\text{FD}} + k_{\text{ID}})$$

$$q_{\text{A}} = k_{\text{FA}}/(k_{\text{FA}} + k_{\text{IA}})$$

is the A* fluorescence quantum yield and

$$q_{\text{D}} = k_{\text{FD}}/(k_{\text{FD}} + k_{\text{ID}})$$

is the D* fluorescence quantum yield. Using eqns. (1) and (2) the following equation is obtained:

[†]Cyclohexane is transparent to $\lambda = 2650 \text{ \AA}$.

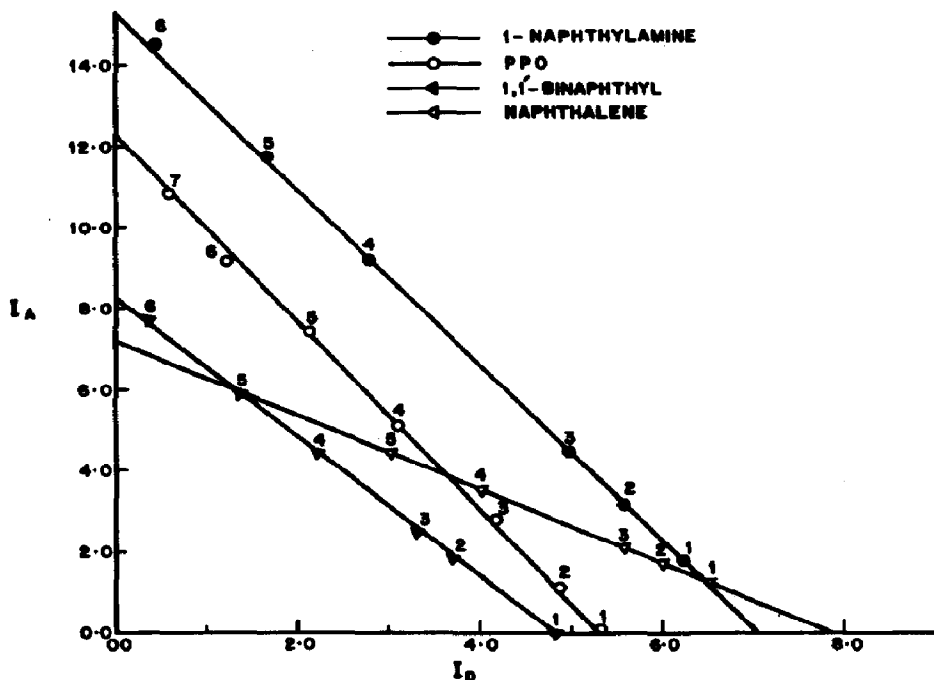


Fig. 2. I_A vs. I_D for 1-naphthylamine $\{0.5 \times 10^{-3}(1) - 3.0 \times 10^{-2}(7) \text{ g l}^{-1}\}$; PPO $\{0(1) - 3.0 \times 10^{-2}(7) \text{ g l}^{-1}\}$, naphthalene $\{4.7 \times 10^{-3}(1) - 3.6 \times 10^{-2}(5) \text{ g l}^{-1}\}$ and 1,1-binaphthyl $\{0.0(1) - 0.1(6) \text{ g l}^{-1}\}$ in cyclohexane at room temperature.

$$I_A/q_A + I_D/q_D = 1 \quad (3)$$

Equation (3) is independent of the concentrations of A or D in the solution. It is valid regardless of the excitation and/or kinetic reaction scheme of A or D as long as both molecules are the only excited species. This was found to be a necessary and sufficient condition for the validity of this equation [11]. The relative fluorescence quantum yields q_A/q_D can be determined experimentally using eqn. (3). Also, if the absolute quantum yield of the donor is known, the absolute quantum yield of different acceptors can be evaluated. In our experiment we used 1,2,4-trimethylbenzene as a common donor and PPO, 1-naphthylamine, POPOP, 1,1-binaphthyl, pyrene, 9,10-dichloroanthracene, naphthalene and 4-biphenyl phenyl ether as acceptors. In all cases, the concentration of the donor was kept at 3 ml l^{-1} while the concentrations of the acceptors varied from very small values up to a certain maximum value but, in general, the concentrations of the acceptors were kept relatively low compared with that of the donor to ensure that nearly all the incident radiation was absorbed by the donor alone. Also, the donor emission spectra overlap part of the acceptor absorption spectra and as a result energy transfer could take place by radiative and/or non-radiative processes [7]. Nevertheless, the nature and type of energy transfer is immaterial for the validity of eqn. (3). A plot of I_A versus I_D is shown in Figs. 2 and 3 for different acceptors. The relative

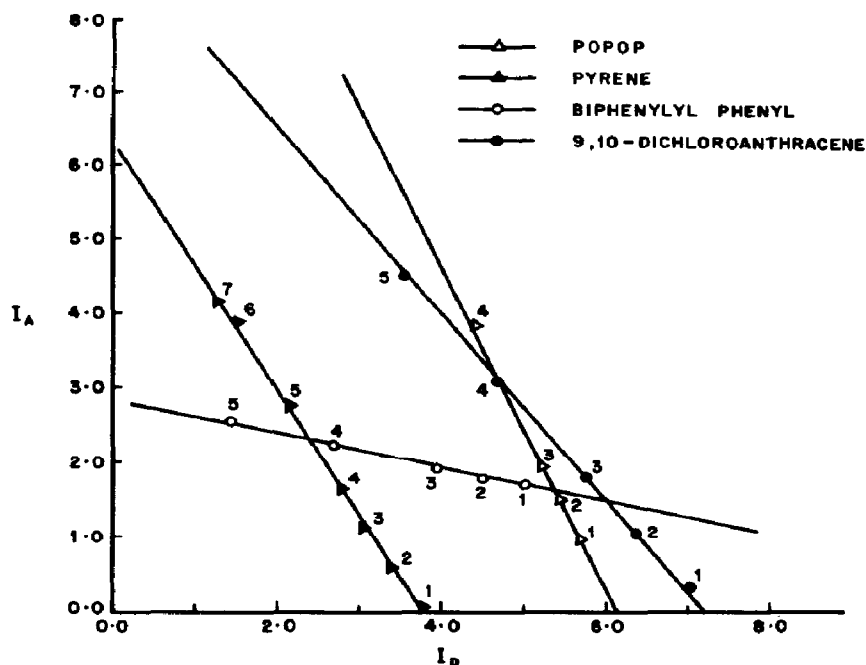


Fig. 3. I_A vs. I_D for POPOP $\{5.0 \times 10^{-3}$ (1) - 2.5×10^{-2} (4) g l^{-1} }, 9,10-dichloroanthracene $\{1.0 \times 10^{-3}$ (1) - 2.0×10^{-2} (5) g l^{-1} }, 4-biphenyl phenyl ether $\{0.93 \times 10^{-2}$ (1) - 5.0×10^{-2} (5) g l^{-1} }, and pyrene $\{0.01$ (1) - 1.5×10^{-2} (7) g l^{-1} in cyclohexane at room temperature.

quantum yields q_A/q_D can be determined from Figs. 2 and 3. The fluorescence quantum yield of the donor was determined relative to 9,10-diphenylanthracene as the standard and was found to be 0.41, identical to the value obtained by Berlman [12]. Using this value for q_A other sets of calibrated graphs were obtained and are shown in Figs. 4 and 5. It is clear from these figures that eqn. (3) is satisfied quite well. The different values for q_A obtained from the intercept of their straight lines with the I_A axis in Figs. 4 and 5 are in very good agreement with the recent values appearing in the literature. This suggests that the energy transfer mechanism could be a useful tool in determining molecular quantum yields in a less troubled and more accurate way than the conventional methods of using standards.

In most of the fluorescence spectra obtained isoemissive points have been observed. This was found to be the case only when the emission of D^* and A^* overlaps, as is clear from Figs. 6 and 7. At this point the intensity of the emission spectra is independent of the concentration C . If one assumes that the isoemissive frequency is ν_0 , then

$$q_A T_A(\nu_0) = q_D T_D(\nu_0) \quad (4)$$

where T_D (or T_A)(ν) is the probability per unit frequency that D^* (or A^*) emits a photon of frequency ν . It is equal to $I_{D(\text{or } A)}(\nu)/\int_0^\infty I_{D(\text{or } A)}(\nu) d\nu$, where $I(\nu)$ is the total emission intensity at frequency ν . Equation (4) was

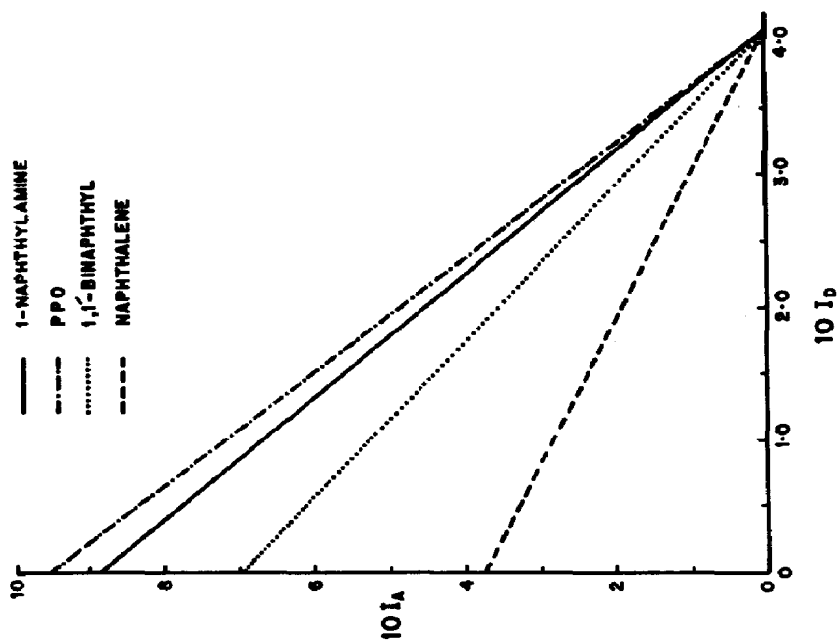


Fig. 4. I_A vs. I_D for the compounds of Fig. 2 assuming that the donor quantum yield is 0.41.

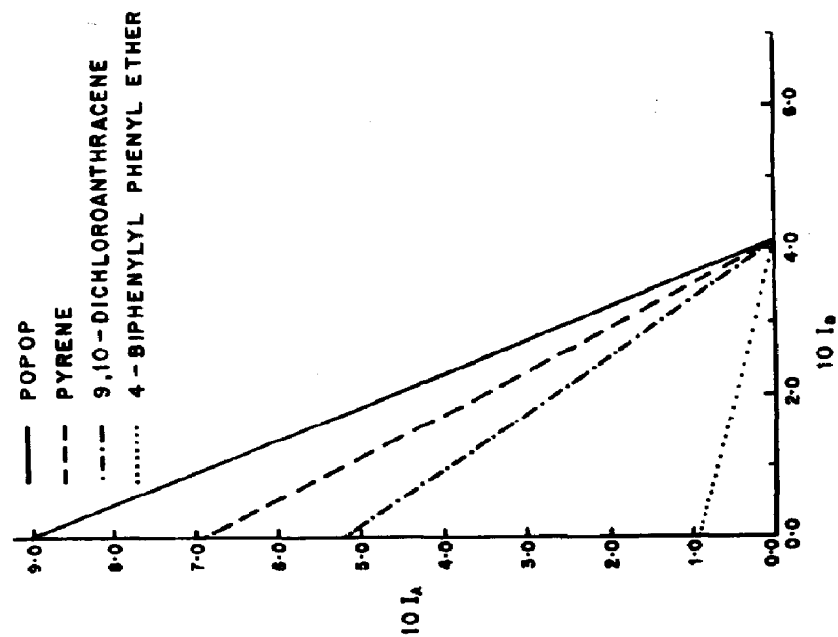


Fig. 5. I_A vs. I_D for the compounds of Fig. 3 assuming that the donor quantum yield is 0.41.

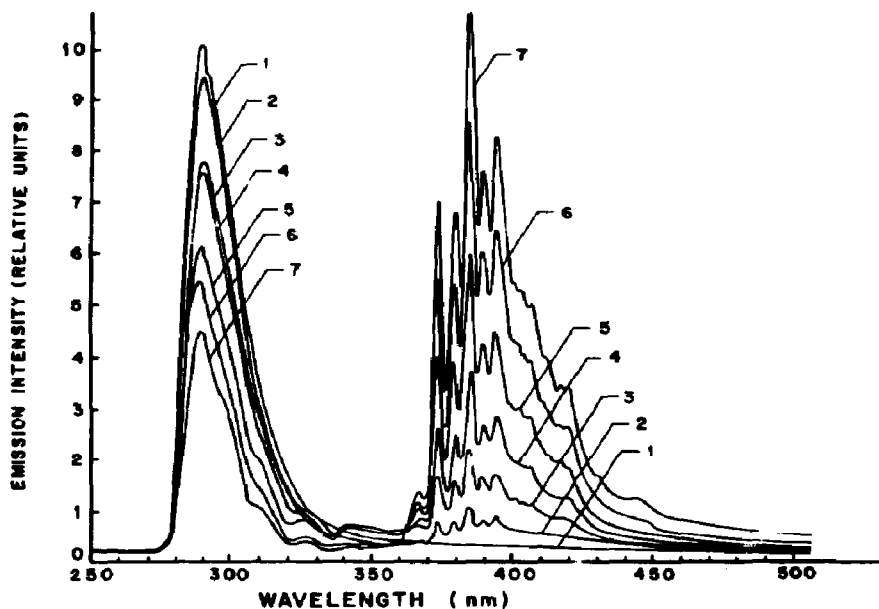


Fig. 6. Fluorescence spectra of 3 ml l^{-1} 1,2,4-trimethylbenzene in cyclohexane (1) alone and with additions of (2) 0.0005, (3) 0.00125, (4) 0.0025, (5) 0.005, (6) 0.01 and (7) 0.015 g l^{-1} pyrene.

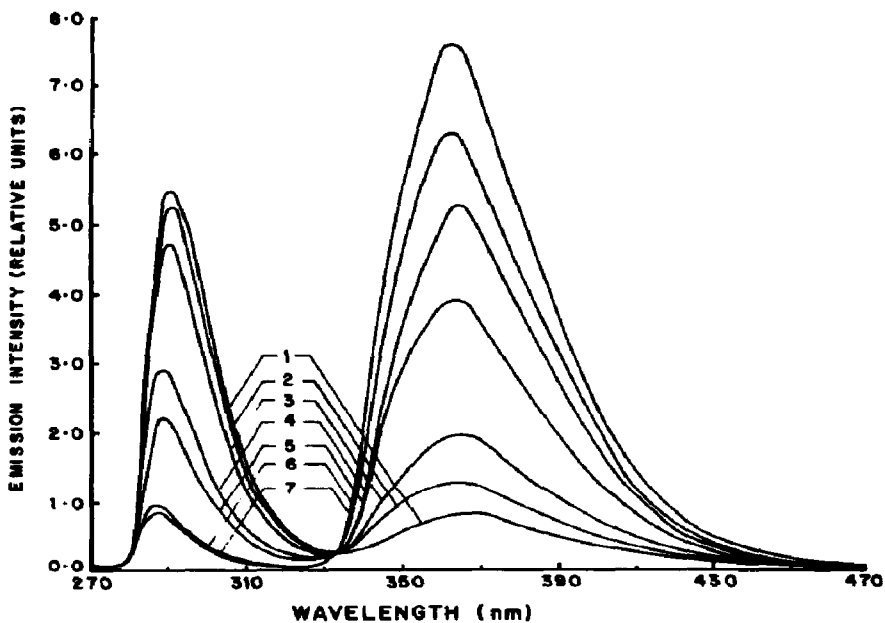


Fig. 7. Fluorescence spectra of 3 ml l^{-1} trimethylbenzene in cyclohexane with additions of (1) 0.0005, (2) 0.0012, (3) 0.0024, (4) 0.006, (5) 0.012, (6) 0.02 and (7) 0.03 g l^{-1} 1-naphthylamine.

also used in determining the ratio q_D/q_A for the compounds whose spectra had isoemissive points. This serves, indirectly, as a double check on the

validity of eqn. (3). The values of q_D/q_A obtained using the isoemissive point were found to be identical to those obtained from eqn. (3).

Finally, we measured the decay times $\tau_{D(\alpha A)}$ of all compounds. Since $\tau_{D(\alpha A)} = 1/\{k_{FD(\alpha A)} + k_{ID(\alpha A)}\}$, the values of $k_{FD(\alpha A)}$ and $k_{ID(\alpha A)}$ can be determined from the measured decay time and the corresponding $q_{D(\alpha A)}$. These values were evaluated and are listed in Table 1; they are also in general agreement with the values obtained by other investigators using different methods. It should be noted that in a few cases the values of the rate parameters obtained by our method disagree with the values obtained by other authors which are cited in Table 1. These minor differences are perhaps due to the different techniques and methods used to obtain those values.

Acknowledgments

The authors wish to thank Dr. R. F. Sárraga, Physics Department, University of Puerto Rico, for the time he spent with the computer program in the first stage of this paper. Also many thanks are due to Mr. L. Blinnchensteff of the Puerto Rico Nuclear Center for handling the computer program we used, and to Dr. M. S. El-Ezaby of Kuwait University for helpful discussions.

This research was supported in part by NIH-Grants No. RR-081103-01 and RR-081103-02 and in part by the U.S. Atomic Energy Commission and Oak Ridge Associated Universities. J. R. L. is an Oak Ridge Graduate Fellow at the University of Puerto Rico at Mayaguez.

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