CONCENTRATION AND SOLVENT EFFECTS ON LUMINESCENCE OF MOLECULES CONTAINED IN RIGID MATRICES

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ABSTRACT — Fluorescence and phosphorescence of cumene and of tryptophan in rigid matrices of methylcyclohexane and ethanol were measured at 77 K as a function of concentration. Efects of photoselection were investigated at various concentrations. The results show that the phosphorescence lifetimes and phosphorescence quantum yields decrease upon concentration for cumene solutions, in which a correlation was established between phosphorescence depolarization and increasing concentration. Phosphorescence decay curves become non-exponential at higer concentrations in the case of cumene solutions.

1 — INTRODUCTION

The understanding of environmental effects on luminescence of molecules contained in rigid glasses is fundamental in photophysical studies carried out at 77 K. Although phosphorescence spectroscopy is a current technique in the study of triplet states of aromatic molecules, the effects of the glassy media on the measured parameters is still open to question [1]. On the other hand, concentration effects [2-3] and photoselection [4] can also bring about new problems in the interpretation of the spectroscopic results. In the present work we have obtained luminescence spectra and phosphorescence lifetimes of isopropylbenzene (cumene) in methylcyclohexane and ethanol glasses at 77 K, changing the concentration from about 0.72 M down to 7.2×10^{-4} M. Special care was put on the investigation of the character of the phophorescence decay curves as a function of either solute concentration, nature of the glassy environment and wavelength peak emission.

For its biological importance the same type of research was undertaken with tryptophan solutions.

The excitation wavelength λ_{ex}, was in general 255 nm for cumene emission spectra and $\lambda_{ex} = 280$ nm for tryptophan.

2 — EXPERIMENTAL DETAILS

Fluorescence, phosphorescence and excitation spectra were measured in a conventional Perkin-Elmer spectrometer. The changes of the degree of polarization, p, for fluorescence and phosphorescence were obtained with a proper set of UV polarizers. Under the experimental conditions used, the value of p is taken [5] as

$$p = \frac{I_{VV} - I_{VH}\,(I_{HV}/I_{HH})}{I_{VV} + I_{VH}\,(I_{HV}/I_{HH})}$$

The subscripts show the orientation of the electric vector (first letter) and emission (second letter), V and H representing the vertical and horizontal orientations. The expression accounts for the eigenpolarization of the apparatus [6] which under our experimental conditions is not negligible, particularly over the longer wavelength region.

The experimental arrangements and nomenclature used for polarization studies is illustrated in Fig. 1.

Dried gaseous nitrogen was circulated inside the sample compartment to avoid some possible condensation on the dewar walls. Most of the samples were uncracked and transparent at 77 K although this is not always the case at higher concentrations, in which signs of turbidity were apparent. Fast-cooled and slow-cooled samples did not produce any appreciable alteration on the measured photophysical parameters. Further details of the experimental procedure used for phosphorescence measurements were previously reported [3].

3 — RESULTS AND DISCUSSION

The kinetic scheme for the most probable unimolecular processes taking place after the excitation of the molecule can be written as follows:

	Process	Rate parameter
Fluorescence	$^{1}M^{\star} \rightarrow {}^{1}M + h\nu_{FM}$	K_{FM}
Internal conversion	$^{1}M^{\star} \rightarrow {}^{1}M$	K_{GM}
Intersystem crossing	$^{1}M^{\star} \rightarrow {}^{3}M^{\star}$	K_{TM}
Phosphorescence	$^{3}M^{\star} \rightarrow {}^{1}M + h\nu_{PT}$	K_{PT}
Intersystem crossing	$^{3}M^{\star} \rightarrow {}^{1}M$	K_{GT}

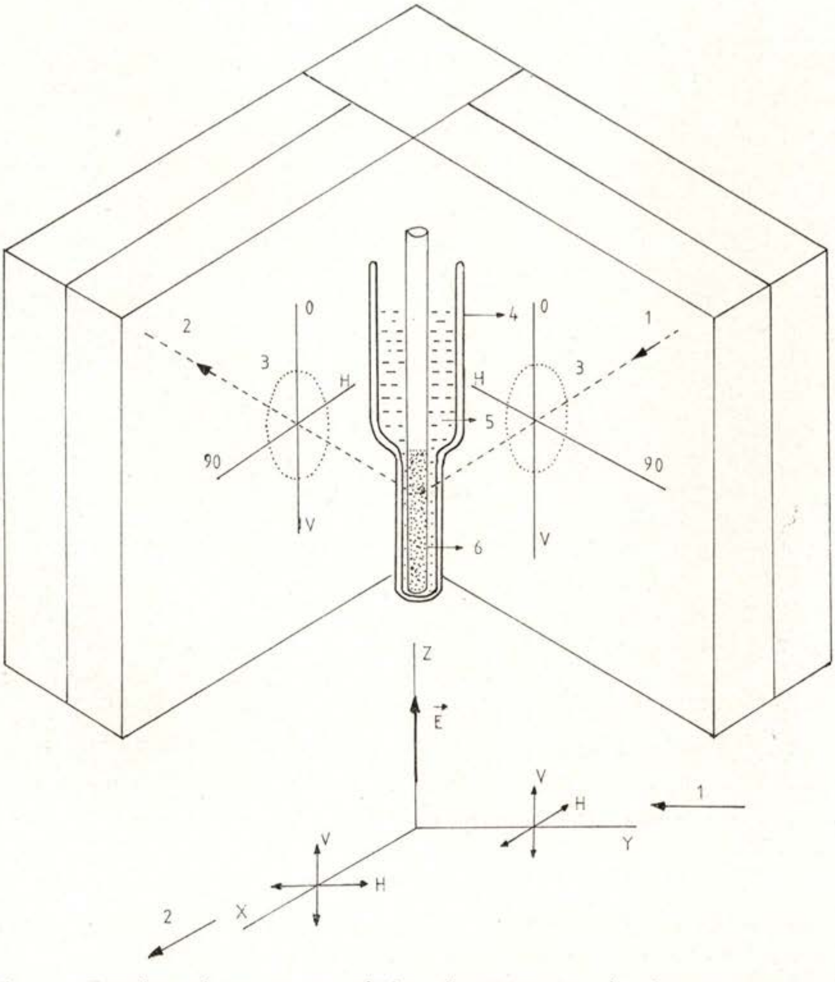

Fig. 1 — Experimental arrangement of the cell compartment for the measurement of polarization luminescence spectra; 1-excitation beam; 2-emission beam; 3-polarizer; 4-quartz dewar; 5-liquid nitrogen; 6-quartz cell; V-vertical orientation of the electric vector, $\vec{E}$; H-horizontal orientation.

The notation used follows the one generally accepted in Organic Luminescence for characterizing the electronic and spin states [7-9].

An example of fluorescence and phophorescence spectra of cumene in methylcyclohexane (7.2×10^{-4} M) in shown in Fig. 2, obtained from a transparent sample, without polarizers. Phosphorescence spectra of the same sample, obtained with the various orientations of both polarizers, are presented in Fig. 3. From the spectra one can conlude that photoselection is not negligible for randomly orientated molecules at 77 K. This implies that the experimental ratio of the phosphorescence quantum yield to fluorescence quantum yield,

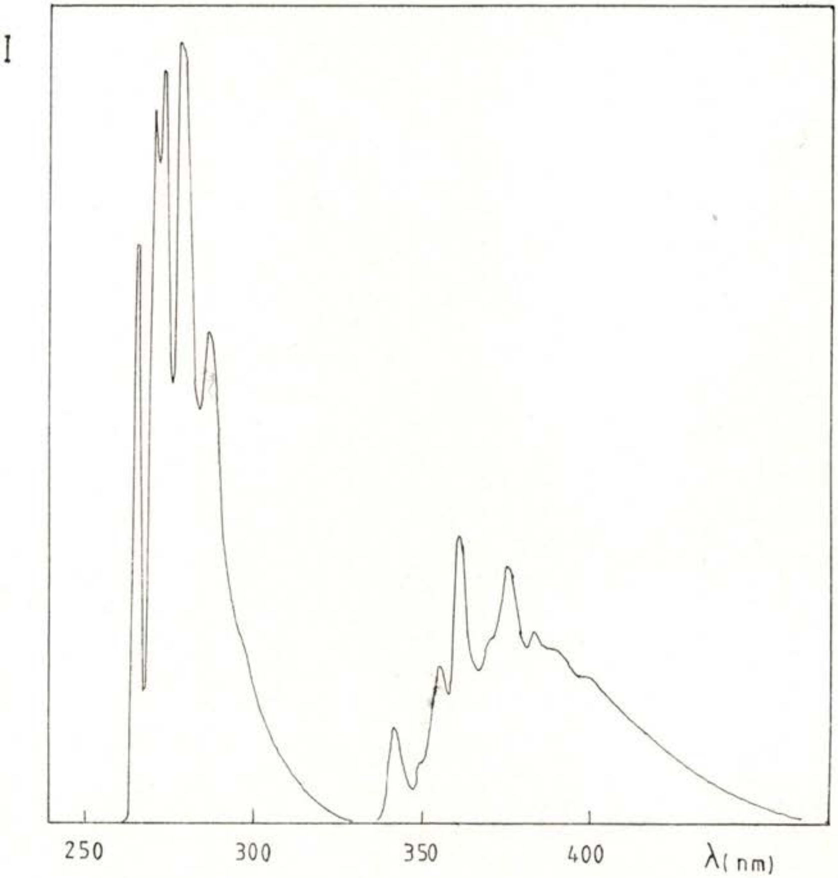

Fig. 2 — Fluorescence and phosphorescence spectra of cumene in methylcyclohexane (7.2×10^{-4}M) at 77K.

$\chi = \phi_{PT} / \phi_{FM}$, measured from spectra obtained without polarizers, can, in fact, introduce some errors as pointed out before [4], [10]. Experimental arrangements to correct for emission anisotropy are, in general, quite complicated for studies carried out at 77 K with glassy solvents [10]. It is therefore advisable to get the correct luminescence values of I_{VH} and I_{VV} for a proper interpretation of the χ values obtained.

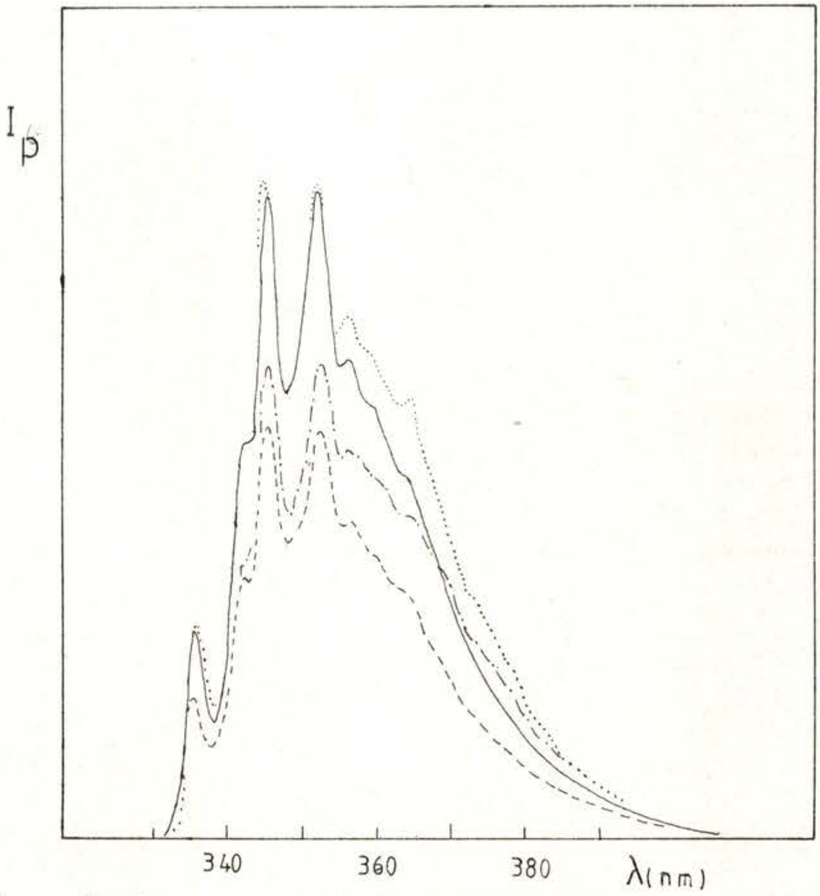

Fig. 3 — Phosphorescence spectra of cumene in methylcyclohexane (7.2×10^{-4}M) for various orientations of the polarizers: HV(—); HH(···); VH(- · -); VV(- -).

Results obtained for cumene solutions in ethanol are listed in Table I. The reported values of phosphorescence litetimes, τ_p, are averages obtained from various recorded decays. The majority of log plots are exponential after the initial intensity has dropped about

TABLE I — Experimental values of χ, τ_p and χ/τ_p of cumene solutions in ethanol, at various concentrations.

C (M)	χ	τ_p (s)	χ/τ_p (s^{-1})
7.2	~0.1	—	—
3.6	~0.1	2.0	—
0.72	0.44	4.0	0.11
0.36	0.56	6.5	0.09
0.14	0.90	7.1	0.13
7.2×10^{-2}	0.94	7.2 ($\lambda_{em} = 376$ nm)	0.13
		7.3 ($\lambda_{em} = 342$ nm)	0.13
		7.0 ($\lambda_{em} = 362$ nm)	
7.2×10^{-3}	1.02	7.5	0.14
7.2×10^{-4}	0.96	7.5	0.13

10–20%. The reproducibility of values is within ± 0.2s. Phosphorescence lifetimes are independent of emission wavelength, λ_{em}, as seen in Table I for 7.2×10^{-2} solutions. In the remaining cases the τ_p values are obtained at $\lambda_{em} = 376$ nm for cumene solutions. In table II we show the values of χ ratios and of τ_p, measured for cumene solutions in methylcyclohexane, as a function of concentra-

TABLE II — Experimental values of χ and τ_p of cumene solutions in ethanol, at various concentrations, without polarizers and with polarizers.

C (M)	χ	τ_p (s) without polarizers	τ_p (s) with polarizers
0.72	0.41		VH-2.8 HV-2.8 VV-2.9 HH-2.8
0.14	0.70	5.0 ($\lambda_{em} = 342$ nm) 5.1 ($\lambda_{em} = 362$ nm) 5.6 ($\lambda_{em} = 376$ nm)	
7.2×10^{-2}	0.74	5.9	
7.2×10^{-3}	0.73	5.9	
7.2×10^{-4}	0.73	6.0	HH-6.0 VH-6.0 VV-5.9 HV-6.0

tion. Results of τ_p obtained with and without polarizers and at various λ_{em}, show no major differences, at a common concentration.

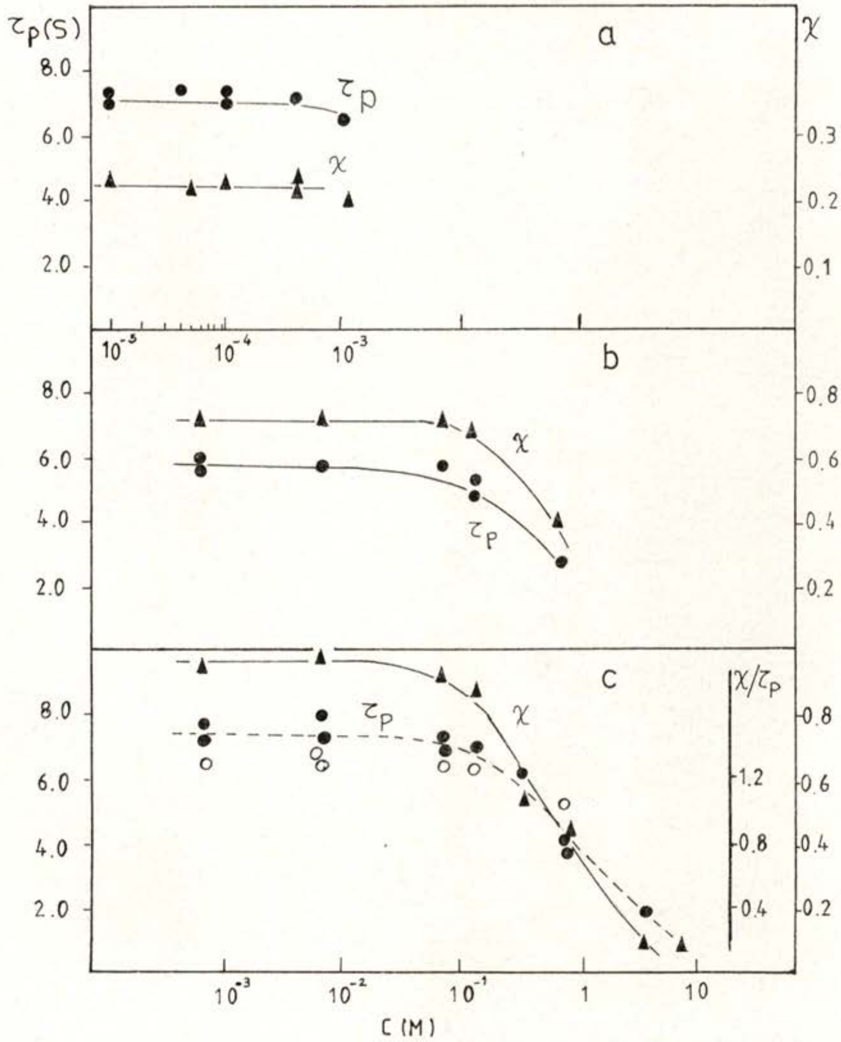

Fig. 4 — Experimental values of χ and τ_p as a function of concentration; a — tryptophan in ethanol; b — cumene in methylcyclohexane; c — cumene in ethanol; (o) represent χ/τ_p.

The results obtained for χ, τ_p and χ/τ_p are summarized in Fig. 4 for tryptophan and cumene solutions, at various concentrations.

Values of τ_p at higher concentrations are of difficult assessment in our experimental set up. A proper phosphoroscope is being constructed in our laboratory for suitable measurements of lifetimes in the milisecond region. However we were able to demonstrate that a decrease of τ_p, ϕ_{PT} and exponentiality of the decays is taking place at higher solute concentrations.

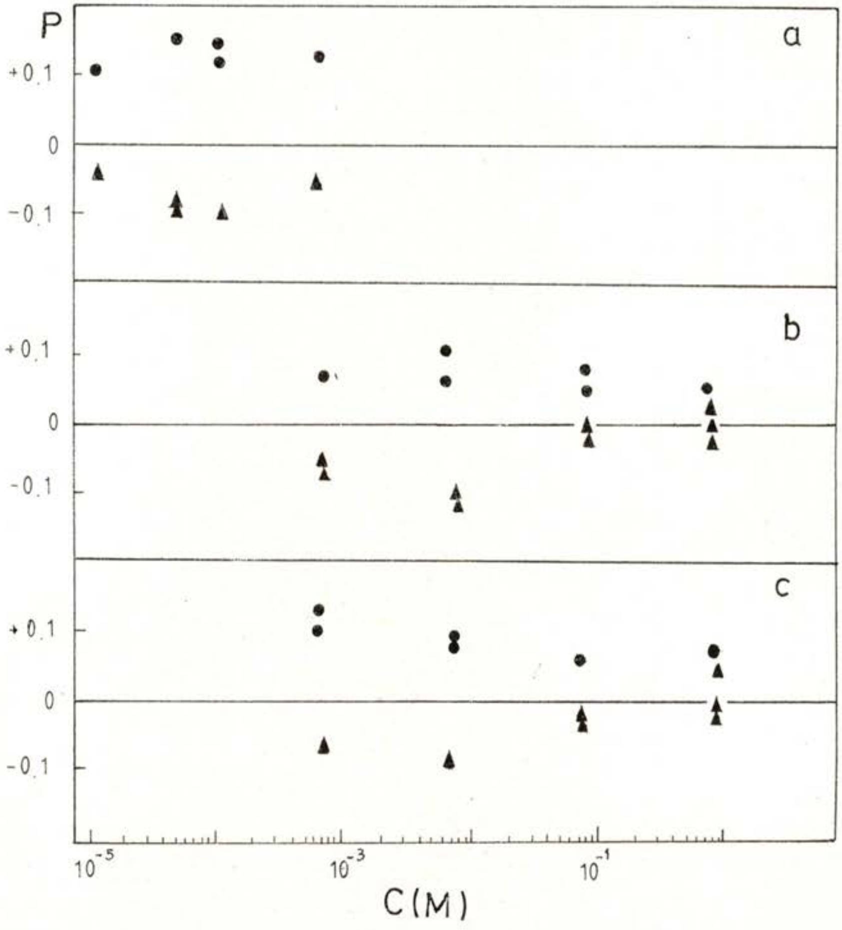

Fig. 5 — Values of luminescence polarization, p, *vs* concentration; a — tryptophan in ethanol, $\lambda_{ex} = 280$ nm, $\lambda_{em} = 311$ nm (•) and $\lambda_{em} = 404$ nm (▲); b — cumene in ethanol, $\lambda_{ex} = 260$ nm, $\lambda_{em} = 274$ nm (•) and $\lambda_{em} = 362$ nm (▲); c — the same as b, for cumene in methylcyclohexane.

The concentration variation of polarization of the same systems are presented in Fig. 5. The values were obtained upon well defined emission bands with weak vibrational overlap. Careful measurements must be taken to ensure good reproducibility during the period of a series of experiments. It was advisable to measure consecutively the luminescence from the various orientations (for example I_{VV}, I_{VH}, I_{HV}, I_{HH}, and then to check again I_{VV}) to be sure

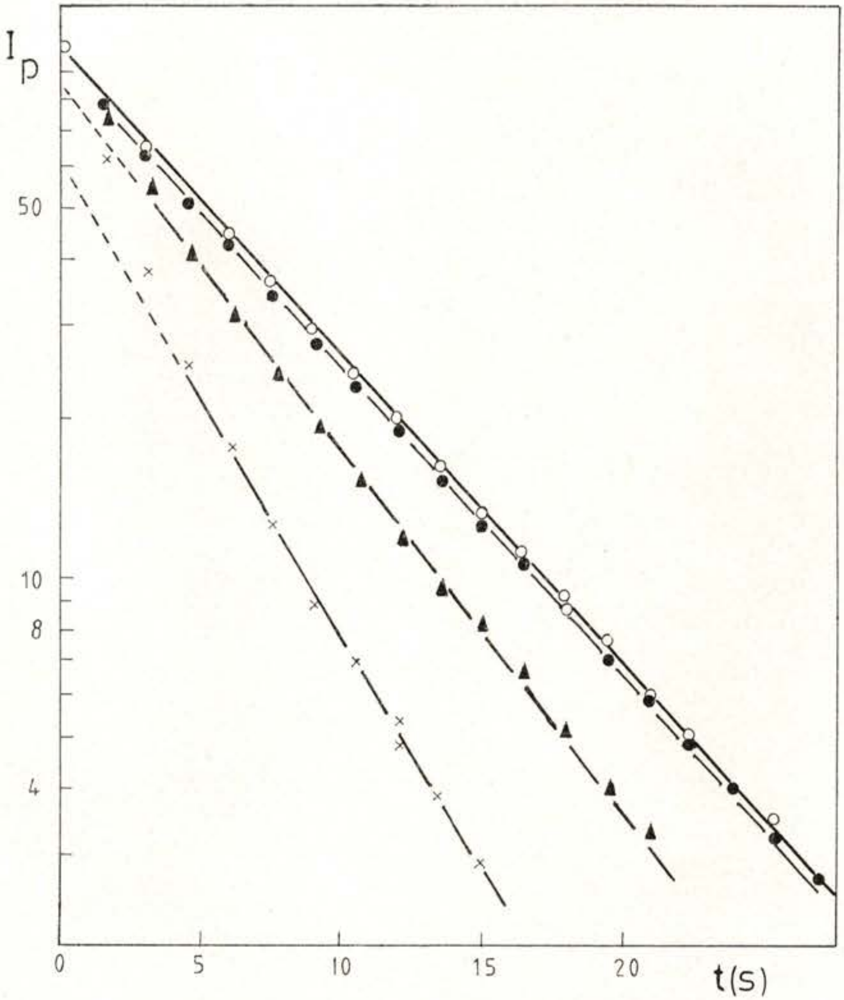

Fig. 6 — Phosphorescence log decays of cumene in ethanol; (o) 7.2×10^{-4}M; (•) 7.2×10^{-3}M; (▲) 0.36M; (×) 0.72M; $I_p = 100$ is a common value to all the decays.

that any alteration had occurred. We can see from Fig. 5 that fluorescence displays a typical « in plane » polarization while an « out of plane » character is found for phosphorescence. Hower this negative polarization for phosphorescence disappears at higher concentrations in cumene solutions.

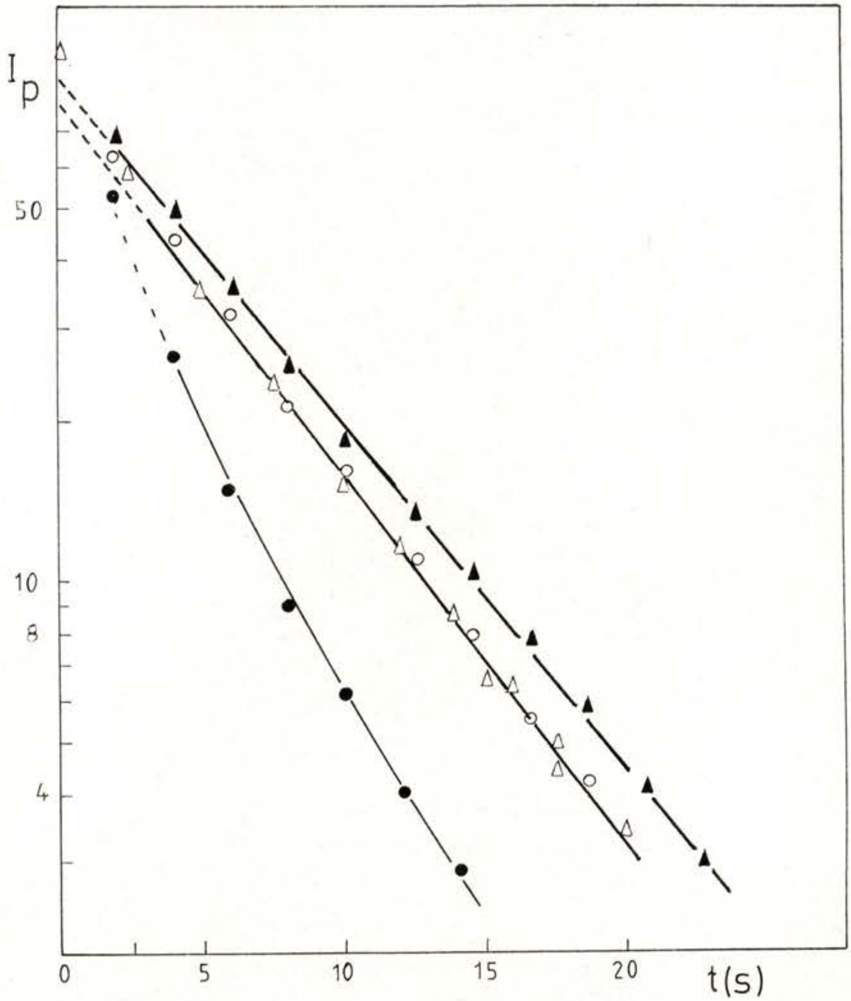

Fig. 7 — Phosphorescence log decays of cumene in methylcyclohexane; (▲) 7.2×10^{-4}M; (o) 7.2×10^{-2}M; (Δ)0.14M; (•)0.72M; $I_p = 100$ is a common value to all the decays.

It is interesting to note that the correlation of phosphorescence depolarization upon concentration is accompanied by an increase of the non-exponential behaviour of the respective decay curves.

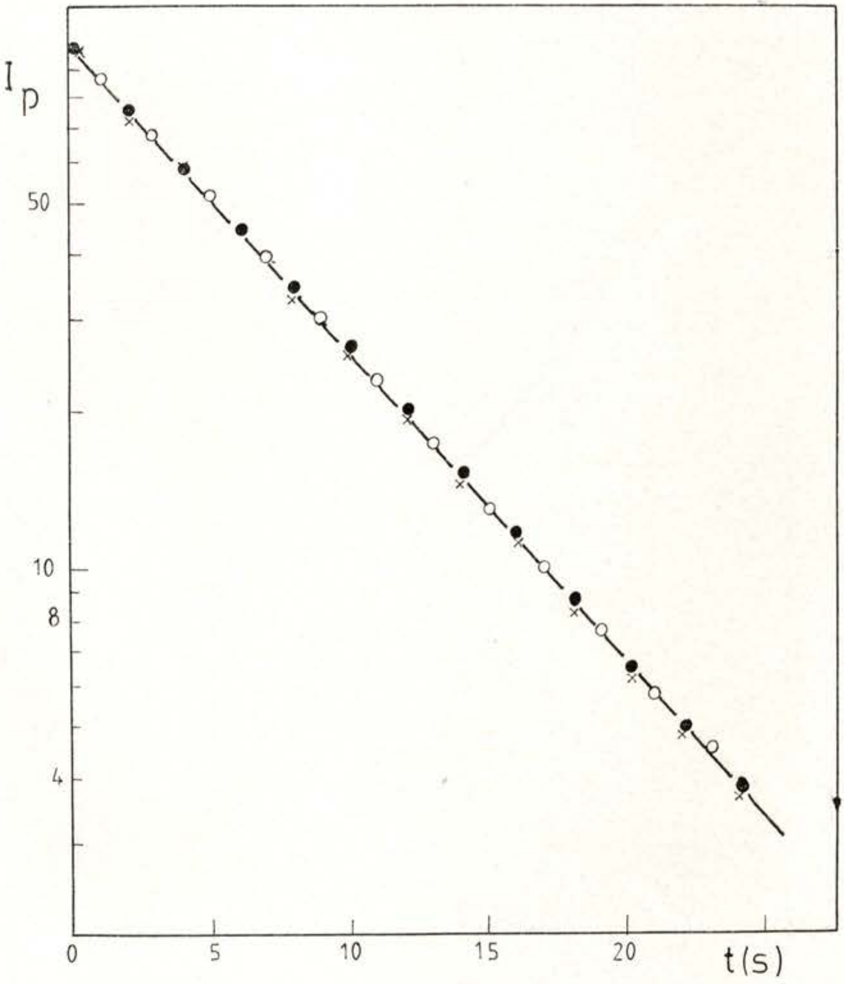

Fig. 8 — Phosphorescence log decays of tryptophan in ethanol; (•) 5×10^{-5}M; (○) 1×10^{-4}M; (×) 1×10^{-3}M.

The character of the various decays as a function of concentration was investigated for cumene in ethanol, cumene in methylcyclohexane and tryptophan in ethanol as shown, respectively, in Figures 6, 7 and 8. The decays displayed at different orientations of the polarizers, for a dilute solution of cumene in methylcyclohexane, show

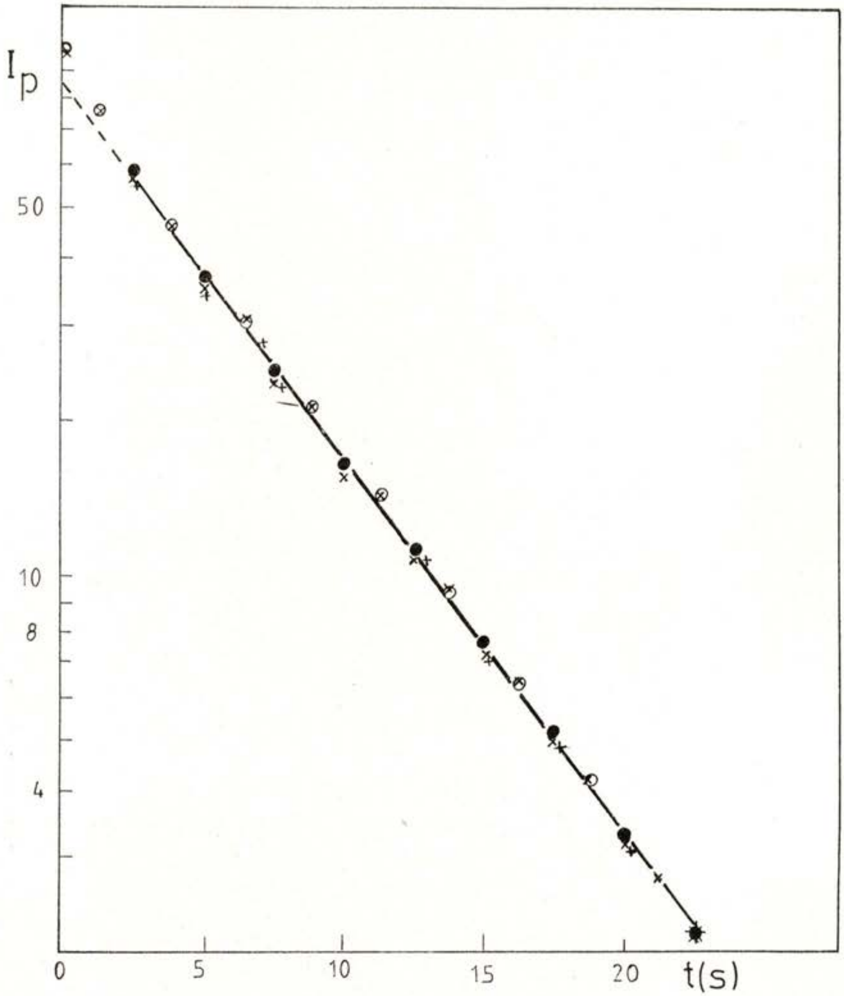

Fig. 9 — Phosphorescence log decays of cumene in methylcyclohexane (7.2×10^{-4}M) at various orientations of the polarizers. HH(•); VH(×); HV(o); VV(+); $I_p = 100$ is common to all the decays.

the same type of behaviour, as illustrated in Fig. 9. One can conclude that the degree of polarization does not change during the phosphorescence decay.

The results of Table I, Table II and Fig. 4 show, for cumene solutions, that not only τ_p and χ decrease upon concentration but the same happens to χ / τ_p. Moreover the phosphorescence intensity drops down to zero at higher concentration. Similar results have been reported with benzene and benzene derivatives [3], [11-12]. In the absence of further deexcitation processes of $^1M^\star$ and $^3M^\star$ the ratio χ is given by

$$\chi = K_{TM}\ K_{PT}\ \tau_p\ K_{FM}^{-1}$$

and the results would indicate that either K_{TM}, K_{PT} or K_{FM} could change upon concentration. An increase in the measured fluorescence quantum yield, ϕ_{FM}, *vs* concentration was reported [11] for a single crystal of benzene but the results obtained require a cautious interpretation. It should be said that an increase of ϕ_{FM} with a decrease of temperature, as found in benzene, is in good agreement with a similar variation of fluorescence lifetime, τ_M, *vs* temperature [13], which implies that K_{FM} is practically constant with temperature, except for its variation due to refractive index differences [14]. On the other hand our results have shown that the ratio χ does not represent the true ratio of phosphorescence to fluorescence yields, due to the fact that a different set of photoselected molecules is viewed from samples with different concentrations. Furthermore the values of τ_p at higher concentrations do not represent a single exponential decay in the case of cumene solutions. It should be noted that the results obtained for tryptophan solutions show that both χ and τ_p are unchanged with concentration and that the phosphorescence decays are all exponential. However the fact that concentrations used are much lower (10^{-3} M to 10^{-5} M) could explain the absence of concentration effects on χ and τ_p of this molecule. This is also true for the polarization results presented in Fig. 9. We can see that p is relatively constant for both fluorescence and phosphorescence of tryptophan solutions (10^{-3}M $-$ 10^{-5}M), while, for cumene, a depolarization is taking place when concentration increases.

Concentration depolarization of phosphorescence has been reported elsewhere [15] for other aromatic molecules, in which the results could be attributed to a triplet-triplet energy transfer mechanism.

Some general conclusions can already be drawn from the results obtained although a proper kinetic analysis is complex and would need further studies at higher concentrations, including 100% solutions. The results illustrate that both concentration and environmental characteristics change considerably the behaviour for the emiting triplet of cumene. This is not the case of tryptophan solutions under our experimental conditions. For that reason we refer our conclusions to cumene results. Phosphorescence lifetimes and triplet decay curves are strongly dependent on concentration and, at a given concentration, they are also influenced by the solvent environment.

Very dilute solutions show a single exponential decay of the phosphorescent molecules in ethanol matrices, while in methylcyclohexane the decay deviates from exponentiality at the same concentration. On the other hand, the triplet is long lived in ethanol when compared to methylcyclohexane. This is probably due to differences of viscosity and or structure of the glasses. The results are compatible with the existence of other (or others) deexcitation channel apart from the usual unimolecular processes. As a matter of fact it seems reasonable to accept that K_{FM}, K_{PT}, K_{GT} and K_{TM} do not depend strongly on the environment, at 77K. Triplet - triplet migration at higher concentrations could well explain both the triplet quenching and luminescence depolarization. However one can not neglect the possibility of the existence of agregation of cumene molecules into microcrystalline regions in which excitonic migration can occur, thus reducing the phosphorescence signal. This hypothesis is also consistent with the non-exponential behaviour of the decays at higher concentrations for which phosphorescence could occur from molecules trapped in non-equivalent sites.

This possibility is in good agreement with the experimental detection of delayed fluorescence in benzene and toluene solid solutions [3] with a suitable phosphoroscope. Broadening of the phosphorescence spectra with increasing concentration, as found in the present work, is also compatible with emission arising from microcrystalline regions.

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