

THERMAL QUENCHING OF SOME LIQUID SCINTILLATORS*

by

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INTRODUCTION

Both the brightness and time response of some liquid scintillators have been found to vary with temperature.¹ In most cases this temperature dependence is attributable to changes in the viscosity of the medium. There are at least two different ways in which changes in viscosity can affect the liquid scintillator properties. In dilute binary liquid scintillators the pulse rise time depends upon the diffusion-controlled transfer of energy from excited solvent molecules to the solute. The effectiveness of intermolecular quenching can also be diffusion limited and therefore dependent upon viscosity, as well as any other bimolecular processes.

Berlman² defines a reference distance, R_0 , for energy transfer from one molecule to another as that distance at which the rate constant for energy transfer from the donor to the acceptor is equal to the rate constant for fluorescence of the donor molecule in the absence of acceptors. A reference concentration, C_0 , is also defined in terms of

*This work was performed under the auspices of the U.S. Department of Energy under Contract No. DE-AC08-83NV10282. NOTE: By acceptance of this article, the publisher and/or recipient acknowledges the U.S. Government's right to retain a nonexclusive royalty-free license in and to any copyright covering this paper.

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R_0 as the concentration at which the probability of energy transfer (as opposed to fluorescence) by the donor is about 75%. For our purposes, a dilute scintillator solution is one with a concentration less than C_0 , in which case the rate of energy transfer is diffusion-limited. If the concentration is greater than C_0 , then the molecules are already, on the average, close enough together for efficient energy transfer, and diffusion becomes less important. The rate of energy transfer decreases as the sixth power of the intermolecular distance, and therefore increases as the square of the concentration, which might be expected for a bimolecular process.

In addition, the effects of solvent viscosity on the quantum yield of dye solutions have been the subject of numerous investigations^{3 4}. This effect is characterized by substantial reductions in the quantum yield and decay time with decreasing viscosity. Investigations to date have centered on binary solutions of the triphenylmethane dyes. Förster and Hoffman⁵ studied a series of such dyes and observed that the quantum yield varies as the 2/3 power of the viscosity (η) for $\eta < 200$ poise. Förster and Hoffman developed a phenomenological model which explains the effect in terms of nonradiative de-excitation caused by the rotation of a phenyl ring about a vinyl bond to an unsaturated carbon atom. The rotation is hindered in viscous media. Subsequent investigators have sought to verify the F-H theory using time-resolved absorption and emission techniques.

We report here the results of effects to utilize viscosity effect to improve the time response of liquid scintillator solutions by studying certain fluorescence emission parameters as a function of temperature. The scintillator solutions studied are summarized in Table 1.

EXPERIMENTAL PROCEDURES

The liquid scintillator samples were contained in 1-cm-thick by 2-cm-diam quartz vials. They were excited with 50-ps (FWHM) pulses of 6-MeV electrons at 360 pulses per second from the DOE/EG&G L-band linear accelerator (linac). Peak electron currents typically ranged from 50 to 500 mA, corresponding to total doses of 0.5 to 5 rads per pulse.

Fluorescent emissions were collected by a quartz lens and focused onto a fast Varian microchannel plate photomultiplier (MCP). The scintillator was viewed at an angle of approximately 135° to the direction of the electron beam to minimize the forward-directed Cerenkov emission. Optical bandpass filters with a FWHM of approximately 50 nm, centered near the emission maximum, were used in all measurements.

Table 1. Summary of scintillator solutions*

Scintillator	Solvent	Shifter	Emitter
I	BA	0.1 M RhB	0.005 M LDS-821
II	BA	0.1 M C-480	0.05 M DCM
III	T	0.027 M PBD	0.22 M TPB
IV	T	0.027 M TP	0.0027 M POPOP

<u>*Abbreviation</u>	<u>Chemical</u>
BA	benzyl alcohol
RhB	Rhodamine B
LDS-821	proprietary dye of Exciton Chemical Company
C-480	Coumarin-480
DCM	4-dicyanomethylene-2-methyl-6-p-dimethylaminostyryl-4H-pyran
T	toluene
PBD	2-phenyl-5-(4-biphenyl)-1,3,4-oxadiazole
TPB	1,1,4,4-tetraphenylbutadiene
TP	p-terphenyl
POPOP	p-bis[2-(5-phenyloxazolyl)]benzene

The MCP output was measured with a sampling oscilloscope, Hewlett-Packard Model 1430A, modified for remote operation of the sampling head near the MCP in the radiation cell. The combined MCP detection system had a response time of 165 ps (FWHM), which was not unfolded from any of our data. The sampling oscilloscope output was digitized, processed, and stored in the linac on-line data processing system based on a dedicated Digital Equipment Corporation PDP-11/34A.

The amount of beam current passing through the scintillator was monitored with a faraday cup placed behind the sample. No attempt has been made to calibrate the sensitivities of these scintillators to an absolute standard. A comparison of some of these liquids, relative to the commercial plastic NE111 has been reported elsewhere.⁶

The samples were electrically heated and the temperature was

controlled by a proportional controller and monitored by a digital thermometer with an immersed stainless steel probe.

Several scintillator pulse parameters are available from the linac on-line data processing system. Those selected for particular attention in this study are the 10% to 90% pulse rise time (RT); the decay time of the back side of the pulse from 0.7 to 0.7/e of maximum intensity (τ_e); and the area under the pulse, or fluorescence efficiency (ϕ), relative to a reference scintillator, usually the plastic, NE111.

A number of the solutions proved to be unstable under the combined effects of elevated temperature and electron flux. To insure the validity of the data at elevated temperatures, the solutions were allowed to cool to room temperature and remeasured. In some instances, the instability precluded reliable measurements above 70°C.

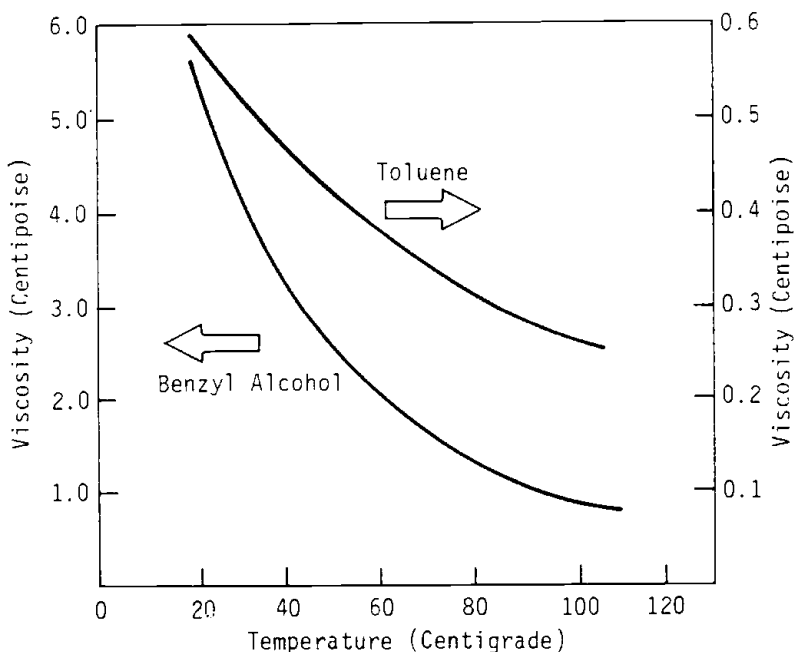


Figure 1. Solvent viscosity versus temperature for toluene and benzyl alcohol

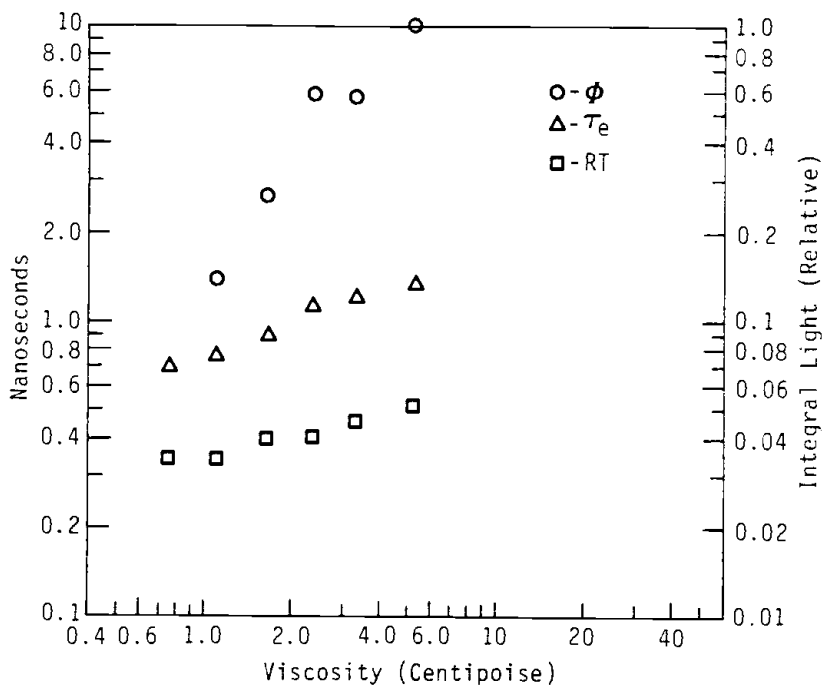


Figure 2. Emission parameters of (I) versus solvent viscosity

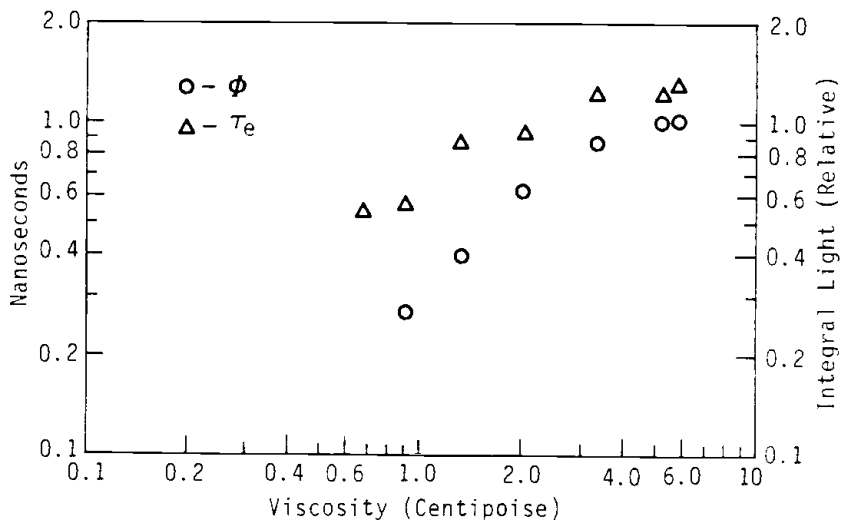


Figure 3. Emission parameters of RhB versus solvent viscosity

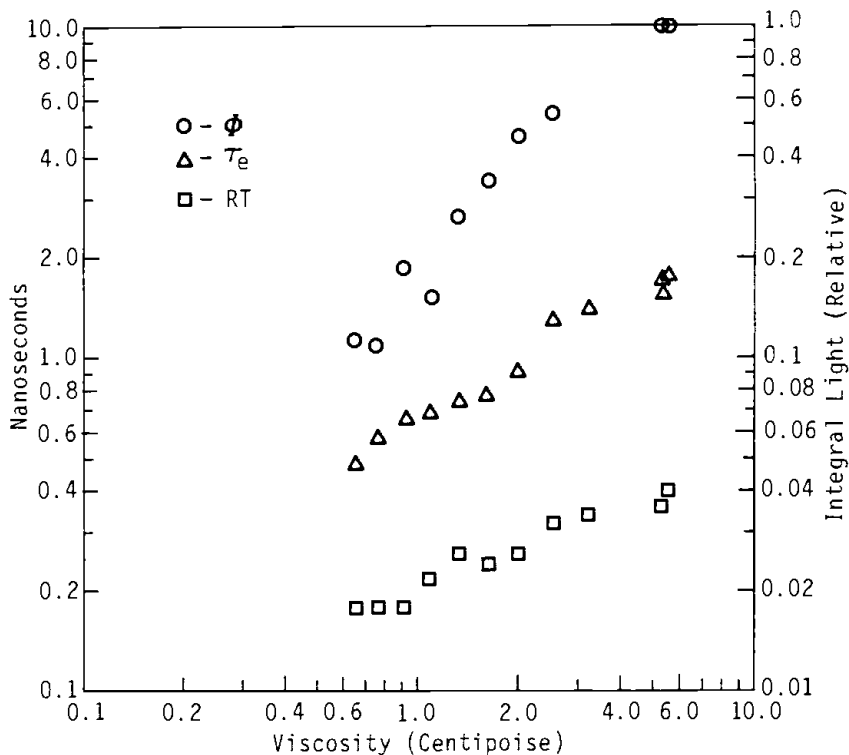


Figure 4. Emission parameters of LDS-821 versus solvent viscosity

RESULTS

It is useful to plot the various fluorescence parameters measured as a function of solvent viscosity. The viscosities of the two solvents, toluene and benzyl alcohol, are plotted in Figure 1 as a function of temperature⁷. Most of the data are plotted as functions of viscosity rather than temperature. It is to be noted that at any given temperature the viscosity of benzyl alcohol is nearly ten times that of toluene.

Scintillator (I)

Figure 2 shows the pulse rise time (RT), τ_e , and ϕ values versus

solvent viscosity for the scintillator (I). Figures 3 and 4 show these parameters for benzyl alcohol solutions of Rhodamine B, the wavelength shifter of scintillator (I), and of LDS-821, the final emitter in (I), respectively. The decay time and efficiency of both the shifter, RhB (Figure 3), and the emitter, LDS-821 (Figure 4) all exhibit negative temperature coefficients. In addition, the slopes of the efficiency and the decay time curves of (I) closely mimic the slopes of the emitter, LDS-821, alone in BA.

The rise time of the ternary system (I) is less dependent upon viscosity than is that of the LDS-821 binary. The high concentration of the wavelength shifter, RhB, in (I) facilitates energy transfer from the solvent to the relatively dilute emitter, thereby making the excitation rate less dependent upon solvent viscosity.

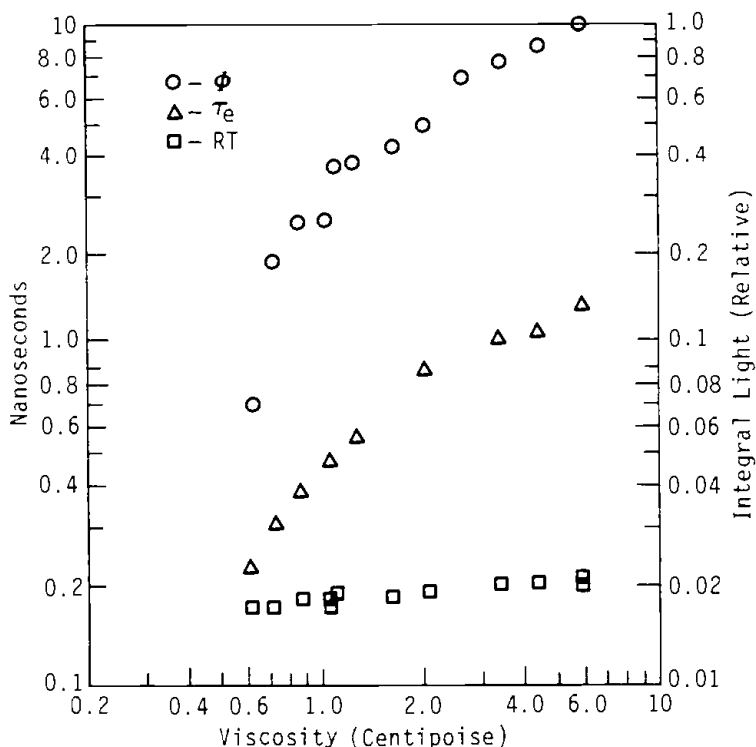


Figure 5. Emission parameters of (II) versus solvent viscosity

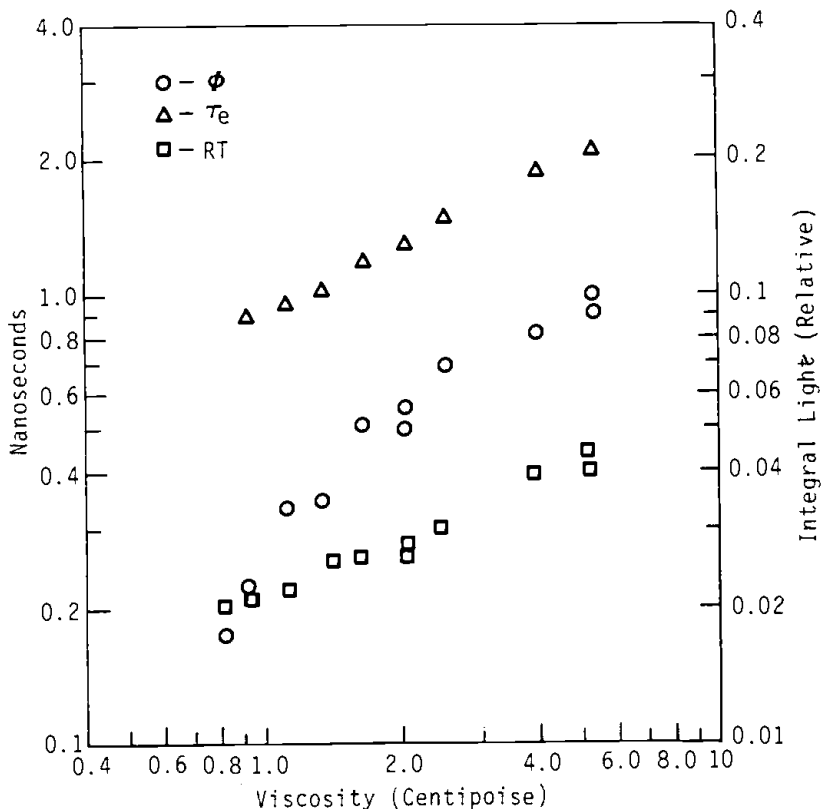


Figure 6. Emission parameters of scintillator (II) with 20% as high a DCM concentration versus solvent viscosity

Scintillator (II)

Figures 5, 6, and 7 respectively, show the time parameters for (II), for a variation of (II) with 20% as much DCM, and for a solution of C-480, the shifter in (II) dissolved in benzyl alcohol.

Again, it is interesting to examine the rise time curves. The ternary system (II) with the higher concentration of DCM (0.05 M), shows very little dependence of the RT on viscosity. Factors other than diffusion are limiting the rise time in this case. However, if one lowers the DCM concentration by a factor of five (Figure 6) one observes a definite dependence of RT on solvent viscosity throughout the region tested. The rise time of the shifter C-480, Figure 7, shows a region of

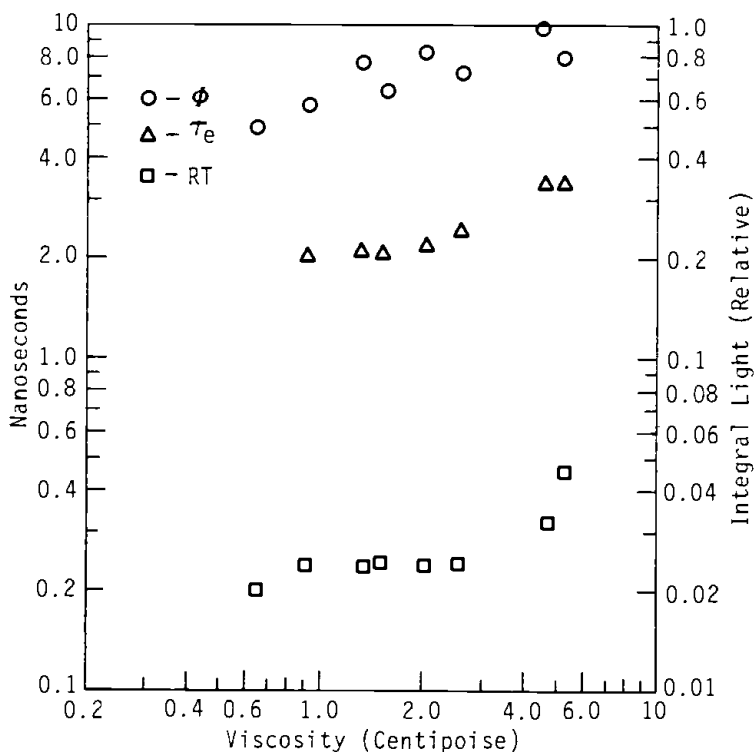


Figure 7. Emission parameters of C-480 versus solvent viscosity

viscosity dependence near room temperature, and then a plateau. Since there is little or no evidence of the plateau or the sharp rise in the RT curve of Figure 6, one can infer that with low concentrations of DCM most of the energy must be passing directly from the solvent to the emitter, by-passing the wavelength shifter. Even at 0.05 M 4-dicyanomethylene-2methyl-6-p-dimethylaminostyryl-4H-pyran (DCM) (Figure 5) the RT values show no indication of the steep increase seen in the C-480 curve near room temperature. This along with the fact that the rise time of (II) is actually faster than the rise of the shifter alone, suggests that the DCM is excited by two different paths, one directly and one through the wavelength shifter, C-480.

From Figures 5 and 6 it can be seen that the viscosity dependence of the decay time is not the same for the two different concentrations

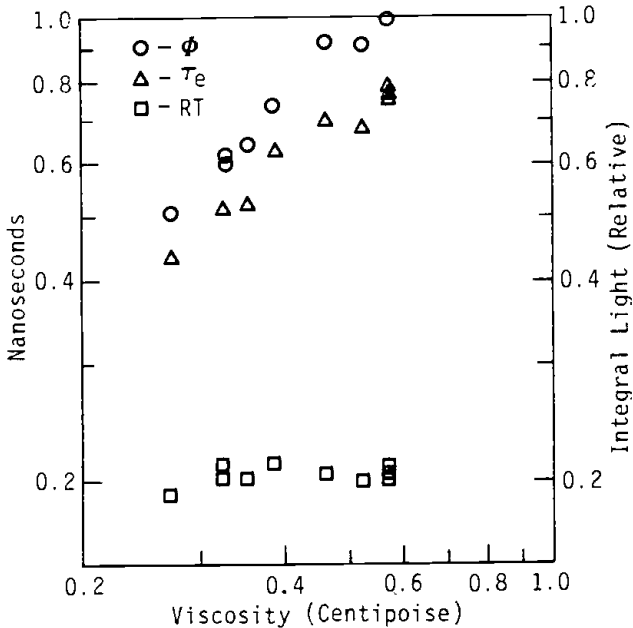


Figure 8. Emission parameters of (III) versus solvent viscosity

of DCM. This is probably related to concentration quenching which like foreign molecule quenching, is a bimolecular process and therefore depends upon solvent viscosity. Lowering the solvent viscosity is analogous to raising the quencher concentration, in that lowered viscosities increase the reaction rates between solute molecules. This effect was observed in our previous work¹ on the thermally-enhanced effect of foreign-molecule quenching in a benzyl alcohol solution of Nile Blue.

Scintillator (III)

Figure 8 shows the pulse parameters of a ternary solution of TPB and PBD in toluene. In the case of this scintillator, the rise time appears to be virtually independent of temperature (or therefore viscosity) over the regions tested. The viscosity of room temperature toluene is comparable to that of benzyl alcohol at 120°C (Figure 1). The rise times of the benzyl alcohol scintillators are also independent of temperature in these regimes.

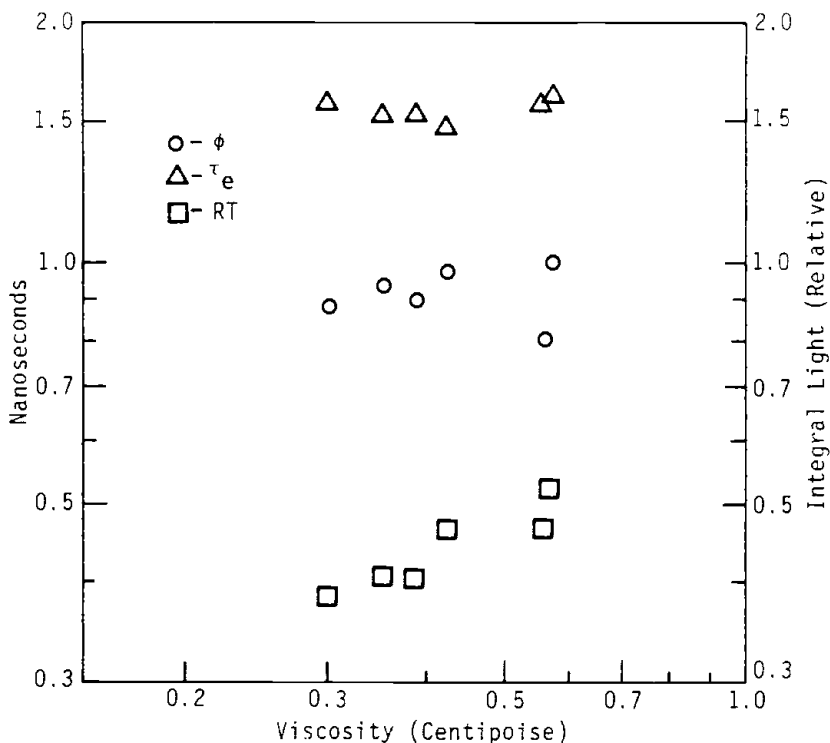


Figure 9. Emission parameters of PBD versus solvent viscosity

Figure 8 reveals a definite dependence of TPB decay time on viscosity, while Figure 9 shows PBD decay to be virtually independent of viscosity. This would be expected for an emitter lacking the special bonding described by Förster and Hoffman.

Scintillator (IV)

Figure 10 shows the pulse parameters of the mixture of TP and POPOP to be essentially independent of viscosity over the range we tested. The solution was stable and the numbers were reproducible. However, when TP was measured alone there was apparent degradation of the solution at a temperature of 70°C. The decay and rise time both degraded at the high temperature and then remained so after the solution was cooled back to room temperature.

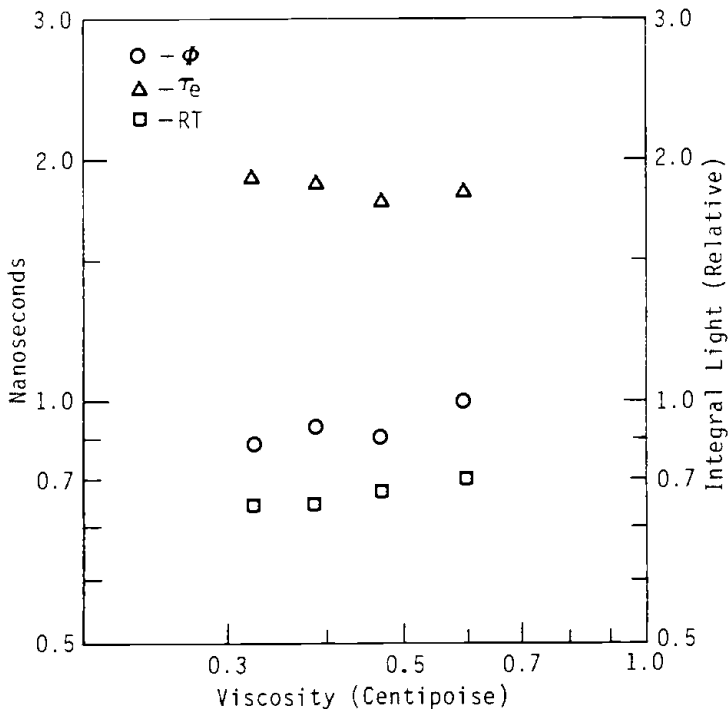


Figure 10. Emission parameters of (IV) versus solvent viscosity

CONCLUSIONS

Heating organic liquid scintillator solutions has proven to be an efficient way to improve the time response in some cases. Higher temperatures increase the rates of diffusion-controlled energy transfer processes in dilute solutions and in solutions with relatively high viscosity at room temperature. Under these conditions both the excitation rate and the rate of intermolecular quenching, including concentration-quenching, become faster at higher temperatures. Except for specific concentration-quenching effects, little temperature dependence of the scintillator pulse parameters was observed in the more concentrated or in the less viscous systems.

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