

A HIGH-Z ORGANIC SCINTILLATION SOLUTION*

by

I.B. Berlman,** L.A. Franks, S.S. Lutz,
J.M. Flournoy, and C.B. Ashford
EG&G, Santa Barbara Operations
Goleta, California 93117

and

P.B. Lyons
University of California
Los Alamos National Laboratory
Los Alamos, New Mexico 87545

INTRODUCTION

It is now believed that the properties needed to make a high-Z liquid scintillator are known. In an earlier study¹, it was demonstrated that a close encounter is a prerequisite for a heavy atom to quench an excited molecule. More recently², it was shown that a very fast scintillator may be obtained by selectively quenching the solute by strategically substituting a relatively heavy atom on the solute chromophore.

In the present experiment, an attempt is made to raise the average Z of a scintillation solution with as little attendant quenching as possible. Since high-Z atoms quench by means of a close encounter, as stated above, such encounters are minimized by the use of alkyl groups substituted on the solvent, solute, and heavy atoms. The aromatic compound 1,2,4-trimethylbenzene (pseudocumene) is used as the solvent; 4,4"-di(5-tridecyl)-p-terphenyl (SG-180) as the solute; and tetrabutyltin as the high-Z material.

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**Presently at Hebrew University, Jerusalem, Israel.

To establish the validity of our ideas, various experiments have been performed with less protected solvents, and heavy atoms. These include benzene, toluene, p-terphenyl, bromobutane, and bromobenzene.

PROCEDURE

Various solutions of p-terphenyl or 4,4"-di(5-tridecyl-p-terphenyl (SG-180) in benzene, toluene, or pseudocumene, were tested. To those solutions, various amounts of a quencher such as tetrabutyltin, bromobenzene, or bromobutane, or of a diluent such as 2,2,4-trimethylpentane (isooctane) were added.

When large quantities of tetrabutyltin were added, there was a diluting of both the solvent and solute. An attempt was made to separate the quenching effect from the dilution effects by substituting isooctane for tetrabutyltin. In addition, the decreases in pulse height are measured with a straight dilution of just the solute by addition of pure solvent.

Before the solutions were tested in a Suprasil spectrometer cell, they were placed in an ultrasonic bath first to dissolve the material and then to outgas the solution.

Each sample solution was evaluated by exposing it to 50-ps electron pulses from the DOE/EG&G electron linear accelerator (linac) and measuring a number of parameters of the resultant fluorescence pulse. These include the 10-90% pulse response rise time (PRT), the pulse full width at half maximum (FWHM), the decay time from 0.7 maximum to $0.7/e$, the integral rise time (IRT) (i.e., the 10-90% rise time of the integral of the pulse), and the integral of the fluorescence pulse (yield). Figure 1 shows a schematic diagram of the experimental arrangement.

Standard solutions were tested each day to assess variations in detection efficiency of the system.

RESULTS

In one set of experiments, our standard was a solution of pseudocumene, as solvent, and SG-180 as solute, at a high concentration of 0.14 M. To this solution, various amounts of tetrabutyltin were added, and the resultant fluorescence

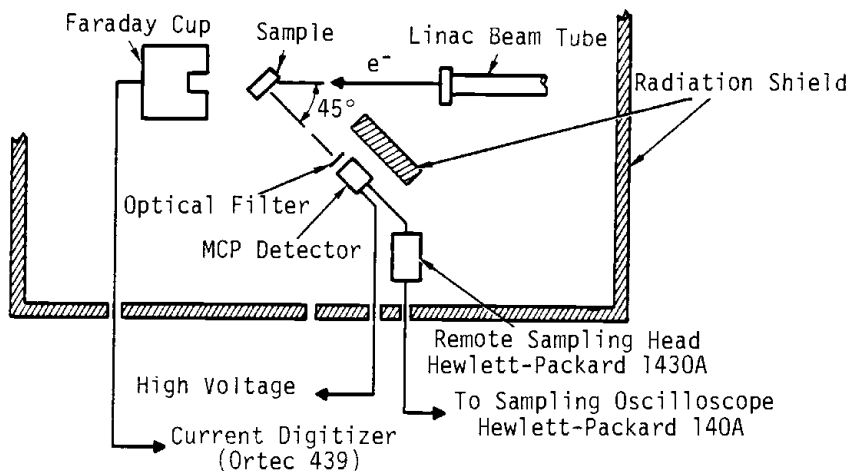


Figure 1. Schematic diagram of test configuration used for scintillator evaluation. Linac was operated at 6 MeV with 50 ps (FWHM) electron pulses at 360 Hz.

Table 1. Quenching by tetrabutyltin in a high-concentration solution of SG-180 in pseudocumene (see Glossary for abbreviations).

SG-180 (moles/liter)*	TBSN (volume %)	PRT (ns)	FWHM (ns)	Decay		Yield**
				Time (ns)	IRT (ns)	
0.14	--	0.51	2.0	1.7	5.9	0.8
0.07	50	0.55	1.9	1.4	4.1	0.3
0.04	75	0.51	2.3	1.6	3.8	0.2

*Takes into account dilution by quencher. Effect of dilution with isooctanes is shown in last three lines of Table 4.

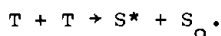
**Yield values from different data sets are not directly comparable due to slight day-to-day variations in detection efficiency.

characteristics were measured. The data are assembled in Table 1.

When tetrabutyltin in a concentration of 75% by volume is added to

the standard solution, the average pulse height is decreased only by a factor of three. This is just a little more than what would be expected from a pure dilution effect where the diluent does not transfer excitation energy to the basic solution. It is of interest to note that the decay time remains essentially unchanged at about 1.6 ns, a result that would indicate that almost no quenching of the solute takes place. Part of the success of this experiment is due to the large solubility of the solute since it does not precipitate out on addition of such large quantities of quencher.

In a second set of experiments, the effectiveness of alkyl chains on the solvent in reducing the quenching by heavy atoms was tested on less concentrated samples than those mentioned above. The data are assembled in Table 2. Most of the pulse parameters show little dependence on TBSN concentration or on the degree of methylation of the solvent. However, the decay time and integral rise time increase somewhat as tetrabutyltin is added. This is probably due to the increased contribution of a long-term decay component. This long component can be explained as being due to delayed fluorescence which in turn is due to two solute triplets combining to give an excited singlet and a ground-state singlet, as indicated below.



High-Z atoms would enhance triplet formation.

In other studies, the effectiveness of alkyl groups in reducing the quenching by a heavy atom was demonstrated by comparing the quenching by tetrabutyltin with that by bromobutane and bromobenzene, compounds with a relatively light atom but with less shielding. As expected, these latter compounds were found to be many times more effective than bromobutane (see Table 3).

The effectiveness of bromobenzene as a quencher may be explained by assuming that it acts as an acceptor of long-range resonant energy transfer from the solvent. This would explain why it is so much more effective than bromobutane and why it is a better quencher of benzene solutions than of toluene or pseudocumene solutions. The spectral characteristics between benzene and bromobenzene are much better

Table 2. Fluorescence characteristics of some scintillation solutions with low solute concentrations quenched by TBSN (see Glossary for abbreviations).

Solute	Concentration (moles/liter)*	Solvent	TBSN (volume%)	PRT (ns)	FWHM (ns)	Decay		Yield**
						Time (ns)	IRT (ns)	
TP	0.025	B	--	0.73	2.7	1.6	4.7	0.52
TP	0.018	B	28.6	--	2.8	1.7	4.6	0.19
TP	0.013	B	50.0	--	3.0	2.0	5.0	0.10
TP	0.025	T	--	0.69	2.4	1.6	4.5	0.37
TP	0.018	T	28.6	0.71	2.6	1.7	4.4	0.15
TP	0.013	T	50.0	0.65	2.9	2.0	5.5	0.08
TP	0.025	PC	--	0.73	2.6	1.7	4.8	0.63
TP	0.018	PC	28.6	0.75	2.8	1.8	4.6	0.29
TP	0.013	PC	50.0	--	3.3	2.2	5.5	0.16
SG-180	0.025	T	--	0.81	2.5	1.6	4.6	0.49
SG-180	0.108	T	28.6	0.81	2.5	1.9	4.5	0.22
SG-180	0.013	T	50.0	0.77	2.9	2.2	4.9	0.11
SG-180	0.025	PC	--	0.75	2.4	1.6	4.7	0.46
SG-180	0.018	PC	28.6	0.83	2.6	1.7	4.6	0.30
SG-180	0.013	PC	50.0	0.71	2.9	2.2	4.9	0.17
4-Br-TP	0.025	PC	--	0.51	1.5	1.0	2.8	0.12
4-Br-TP	0.018	PC	28.6	0.55	1.6	1.3	3.3	0.06
4-Br-TP	0.013	PC	50.0	0.41	1.5	1.9	4.8	0.04
3-Br-TP	0.025	PC	--	0.53	1.6	1.2	3.6	0.17
3-Br-TP	0.018	PC	28.6	--	1.6	1.4	3.5	0.09
3-Br-TP	0.013	PC	50.0	--	1.6	1.5	4.4	0.05

*Takes into account dilution by quencher

**Yield values from different data sets are not directly comparable due to day-to-day variations in detection efficiency.

matched than those between pseudocumene and bromobenzene.

In an effort to separate the solvent dilution effects, a series of experiments were undertaken in which 2,2,4-trimethylpentane (isooctane) was added instead of the tetrabutyltin. In most of the results, summarized in Table 4, this dilution effect was smaller than

Table 3. Fluorescence quenching by bromobenzene and bromobutane (see Glossary for abbreviations).

Solute	Concentration* (moles/liter)	Solvent	Quencher	Concentration (volume %)	PRT (ns)	FWHM† (ns)	Decay Time (ns)	IRT (ns)	yield**
TP	0.025	B	--	--	0.73	2.7	1.7	4.8	0.47
TP	0.025	B	BrBt	1	0.73	2.6	1.6	4.8	0.40
TP	0.025	B	BrBt	2	0.71	2.6	1.6	4.6	0.37
TP	0.025	B	--	--	0.73	2.7	1.7	4.8	0.47
TP	0.025	B	BrBz	1	0.57	1.8	1.4	3.6	0.16
TP	0.025	B	BrBz	2	0.49	1.6	1.2	3.1	0.09
TP	0.025	T	--	--	0.73	2.5	1.6	4.6	0.57
TP	0.025	T	BrBt	1	0.71	2.5	1.6	4.7	0.48
TP	0.025	T	BrBt	2	0.71	2.5	1.6	3.6	0.43
TP	0.025	T	--	--	0.71	2.5	1.6	4.5	0.56
TP	0.025	T	BrBz	1	0.57	2.0	1.4	3.3	0.23
TP	0.025	T	BrBz	2	0.57	1.8	1.5	3.9	0.16
TP	0.025	PC	--	--	0.73	2.5	1.7	4.9	0.40
TP	0.025	PC	BrBt	1	0.73	2.4	1.6	4.4	0.35
TP	0.025	PC	BrBt	2	0.71	2.4	1.6	4.5	0.29
TP	0.025	PC	--	--	0.73	2.5	1.7	4.9	0.40
TP	0.025	PC	BrBz	1	0.63	2.2	1.5	3.9	0.22
TP	0.025	PC	BrBz	2	0.61	2.0	1.5	3.8	0.16
SG-180	0.025	B	--	--	0.77	2.5	1.6	4.6	0.40
SG-180	0.025	B	BrBt	1	0.77	2.5	1.6	4.5	0.35
SG-180	0.025	B	BrBt	2	0.75	2.5	1.6	4.5	0.31
SG-180	0.025	B	--	--	0.77	2.6	1.6	4.6	0.40
SG-180	0.025	B	BrBz	1	0.61	2.0	1.5	3.6	0.17
SG-180	0.025	B	BrBz	2	0.55	1.7	1.2	3.8	0.09
SG-180	0.025	PC	--	--	0.71	2.4	1.6	4.6	0.49
SG-180	0.025	PC	BrBt	1	0.69	2.3	1.5	4.1	0.41
SG-180	0.025	PC	BrBt	2	0.71	2.3	1.5	4.0	0.35
SG-180	0.025	PC	--	--	0.71	2.4	1.6	4.6	0.49
SG-180	0.025	PC	BrBz	1	0.67	2.1	1.4	3.8	0.28
SG-180	0.025	PC	BrBz	2	0.61	1.9	1.4	3.4	0.20

*Takes into account dilution by quencher.

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Table 4. Modification in fluorescence characteristics induced by dilution with isooctane (see Glossary for abbreviations).

Solute	Concentration (moles/liter)*	Solvent	Isooctane (volume%)	PRT (ns)	FWHM (ns)	Decay		Yield**
						Time (ns)	IRT (ns)	
TP	0.025	B	--	0.73	2.7	1.7	4.8	0.54
TP	0.018	B	28.6	0.81	2.9	1.8	4.8	0.40
TP	0.013	B	50.0	0.81	3.3	2.2	5.5	0.29
TP	0.025	T	--	0.71	2.4	1.6	4.8	0.41
TP	0.018	T	28.6	0.79	2.7	1.7	4.7	0.33
TP	0.013	T	50.0	0.91	3.1	2.0	5.2	0.26
TP	0.025	PC	--	0.73	2.7	1.7	5.0	0.61
TP	0.018	PC	28.6	0.79	2.9	1.9	5.0	0.52
TP	0.013	PC	0.50	0.91	3.4	2.4	5.6	0.42
SG-180	0.025	B	--	0.77	2.8	1.6	4.5	0.72
SG-180	0.018	B	28.6	0.77	3.3	2.2	5.3	0.46
SG-180	0.013	B	50.0	0.71	3.9	3.4	6.7	0.26
SG-180	0.025	T	--	0.73	2.5	1.5	4.3	0.87
SG-180	0.018	T	28.6	0.83	3.2	2.0	5.2	0.60
SG-180	0.013	T	50.0	0.85	3.9	3.2	6.4	0.36
SG-180	0.025	PC	--	0.69	2.5	1.6	4.5	1.04
SG-180	0.018	PC	28.6	0.81	3.1	1.9	4.0	0.75
SG-180	0.013	PC	50.0	0.89	3.8	3.2	6.7	0.50
SG-180	0.140	PC	--	0.51	2.0	1.7	5.9	0.84
SG-180	0.070	PC	50.0	0.57	2.2	1.6	5.1	0.72
SG-180	0.040	PC	75.0	0.65	2.5	1.6	4.7	0.52

*Takes into account dilution by isooctane.

**Yield values from different data sets are not directly comparable due to day-to-day variations in detection efficiency.

expected, indicating that isooctane is not necessarily inert as a scintillator solvent. Also, a test of SG-180 in 100% isooctane yielded 20% as much light as the same concentration of SG-180 in benzene, or 14% as much light as SG-180 in pseudocumene, confirming that isooctane was not as inert a diluent as was expected.

The variation in the integral light output (yield) of four

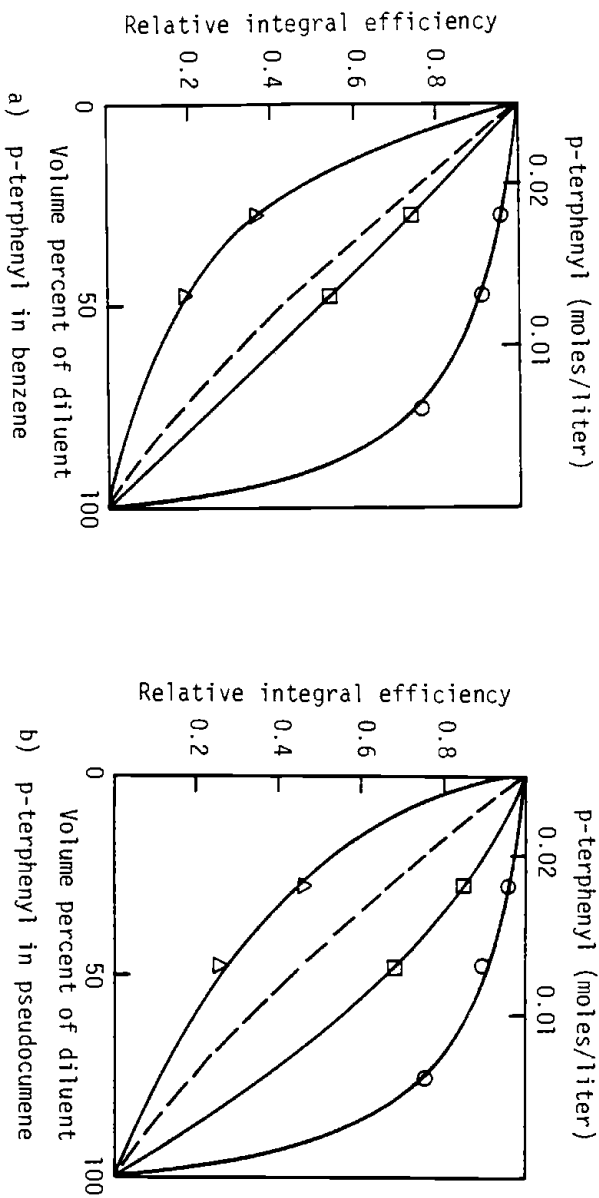


Figure 2. Dilution and quenching effects on light yield of initially 0.025 M solutions of p-terphenyl in benzene (2a) and pseudocumene (2b). Solutions were diluted with benzene (2a-circles), or pseudocumene (2b-circles), isooctane (squares), and tetrabutyltin (triangles) and irradiated with 50-ps burst of 6-MeV electrons. Dashed curve represents effect expected from diluting both solvent and solute with an inert solvent.

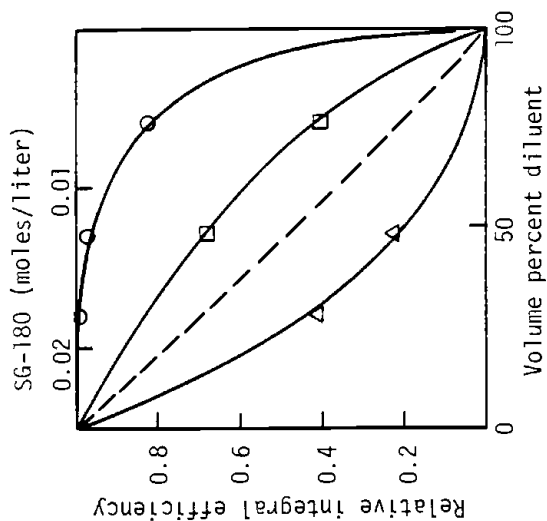
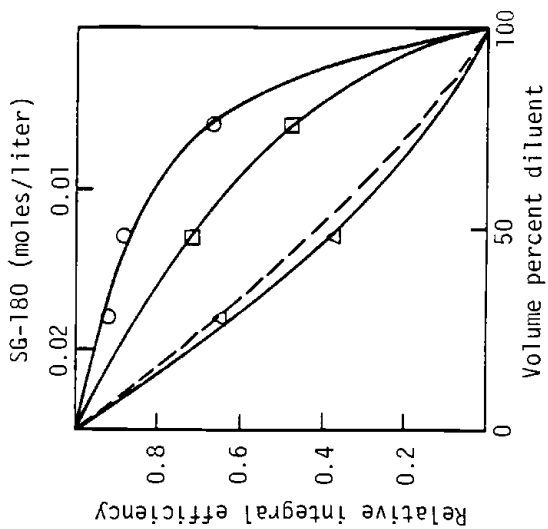


Figure 3. Dilution and quenching effects on the light yield of initially 0.025 M solutions of SG-180 in toluene (3a) and pseudocumene (3b). Solutions were diluted in toluene (3a-circles) or pseudocumene (3b-circles), isooctane (squares), and tetrabutyltin (triangles) and irradiated with 50-ps burst of 6-MeV electrons. Dashed curve represents effect expected from diluting both solvent and solute with an inert solution.

solutions (p-terphenyl in pseudocumene and benzene, and SG-180 in toluene and pseudocumene) as each is diluted with large volumes of the solvent, isooctane, and tetrabutyltin is shown in Figures 2a,b and 3a,b. The yields in each case are normalized to their undiluted values. The dashed curves represent the expected yield if both the solute and solvent are diluted by an inert solvent. Curves above the dashed line represent varying degrees of energy transfer; curves below the dashed line indicate quenching.

Isooctane is seen to be an active diluent for both p-terphenyl and SG-180 in all solvents. The effect is greatest in the case of SG-180 in pseudocumene and is least with p-terphenyl in benzene, where the diluent is nearly inert. These results suggest a selective interaction between the isooctane and methyl groups on the solvent. In fact, addition of only 2% pseudocumene to an isooctane solution of SG-180 increased the yield by 50%. If the yield had varied linearly with the composition between pure pseudocumene and pure isooctane, only a 12% increase should have occurred. It is also noted that the tetrabutyltin quenches the benzene and toluene solutions to a greater degree than those with pseudocumene. The SG-180 solution in pseudocumene was quenched the least. While 50% added tetrabutyltin caused about 80% reduction in the yield of p-terphenyl in benzene, only 1% added bromobenzene produced the same effect. Thus, the combined shielding of the butyl groups on the tin and the tridecyl groups on SG-180 essentially eliminate quenching by the tin.

Figure 4 shows a pulse height spectrum (and associated photopeak) that was obtained when a solution consisting of 0.035 M of SG-180 in 25% by volume of pseudocumene and 75% by volume of tetrabutyltin was exposed to a ⁵⁷Co source. For comparison, the pulse height spectrum from a 0.14 M SG-180 solution in pseudocumene without added tin is also shown. The enhanced photoelectric interaction resulting from the tin is evident and suggests immediate applications to x-ray diagnostics.

ACKNOWLEDGEMENT

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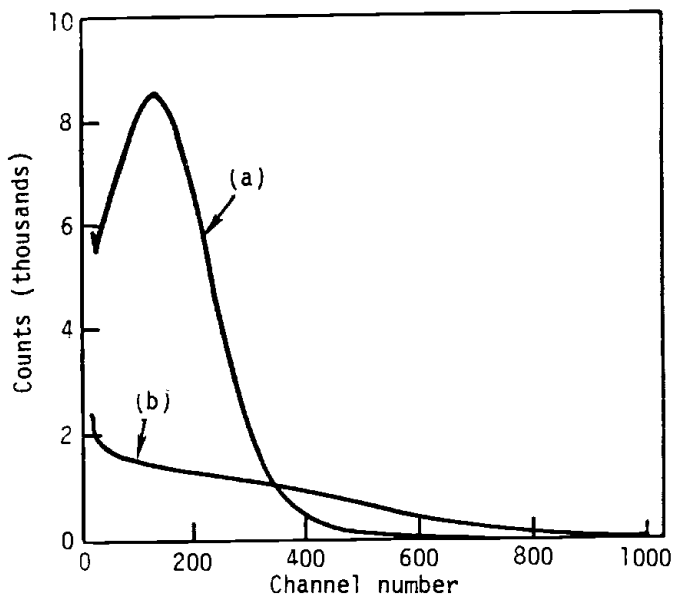


Figure 4. Pulse height spectra from irradiation with ^{57}Co (122 keV gamma-ray) of (a) 0.035 M SG-180 in a solvent of 25% pseudocumene and 75% tetrabutyltin (19% tin by weight) and (b) 0.14 M SG-180 in pseudocumene without added tin. Abscissa is not energy-calibrated.

REFERENCES

1. I.B. Berlman, "Empirical Study of Heavy Atom Collisional Quenching of the Fluorescence State of Aromatic Compounds in Solution", *J. Phys. Chem.*, 77, pp 562-567 (1973).
2. I.B. Berlman, L.A. Franks, S.S. Lutz, J.M. Flournoy and C.B. Ashford, "New Brominated Para Terphenyl for Fast Scintillator Applications", to be published.
3. F. Hirayama and S. Lipsky, "Fluorescence of Saturated Hydrocarbons", *J. Chem. Phys.* 51, p 3616 (1969).
4. F. Hirayama, W. Rothman and S. Lipsky, "Fluorescence of Saturated Hydrocarbons II: The Effect of Alkyl Substituents", *Chem. Phys. Lett.*, 5, pp 296-298 (1970).