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Performance Parameters of some New Efficient and highly soluble Solutes for Liquid Scintillators

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1. Introduction

In the use of fluorescing organic compounds as solutes for liquid scintillators several factors must be considered. The photon yield of the scintillators must be high, the spectral matching to the photo-multiplier sufficient and the fluorescence decay time should be short. Besides these physical properties also some practical requirements must be fulfilled. The solubility in the solvent used should be high and the scintillator should be as little affected by quenching agents as possible. For convenience in handling and sufficient shelf life of the solutions, the photochemical degradation of the scintillator must be negligible.

In this paper the results of systematic investigations on unsubstituted and alkyl-substituted benzoxazole, benzoxazolyl-thiophene and 1,3,4-oxadiazole derivatives will be presented. The measurements of the physical and practical properties of some selected compounds of these series indicate them to be efficient primary or secondary solutes for liquid and also for plastic scintillators.

2. Problems concerning the solubility

The insufficient solubility of many fluorescing organic compounds is known to be a severe limiting factor in their use as scintillator solutes. A vast number of potential solutes with high photon yield give solutions that saturate well below the optimum concentration, c_0 . Therefore, the maximum photon yield cannot be reached under measuring

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conditions. For this reason, the solubility limit, c_s , of an efficient solute should lie well above c_0 .





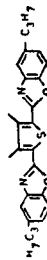
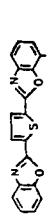


The solubility of an organic compound in an organic solvent depends not only on the lattice energy in the pure solute, but also on the solvent-solute interactions. So far no complete theoretical explanation of solubility of organic compounds exists, which would consider, in addition to the energetics, also the changes in entropy during the dissolution process. However, there are some "rules of thumb", which often enable one to influence the solubility by structural modifications in a given class of compounds. The solubility of organic compounds in non-polar hydrocarbon solvents, for example, can be increased by substituting one or more alkyl groups in appropriate positions or by branching of the aliphatic chains.

The only systematic investigations concerning the solubilization of organic scintillators have been carried out by Wirth¹⁻³. Wirth could increase significantly the solubility of the *p*-oligophenylenes in toluene by substituting methyl, methoxy, and later other straightchain and branched alkyl and alkoxy groups. A slight improvement of the solubility of POPOP has been accomplished by Walker and Waugh⁴ and Vasvari⁵ in a similar manner. However, it must be pointed out, that such general rules have many exceptions, as will be outlined.

During our investigations on aromatic and heterocyclic fluorescing compounds we have directed our attention also to some new benzoxazole, benzoxazolyl-thiophene and 1,3,4-oxadiazole derivatives as potential scintillation solutes.^{6,7} In Table 1a the solubilities and the spectral properties of various derivatives of the benzoxazolyl-thiophene series are summarized. The introduction of two or more methyl groups lowers the solubility of the basic compound instead of increasing it as it might be expected from the rule mentioned before (cf. the compounds I, II, III and IV). On the contrary, the solubilities increase sharply by introduction of branched alkyls, such as isopropyl (V) or sec-butyl (VI) groups. Especially the tert-butyl groups have been found suitable for the solubilization. Disubstituted benzoxazolyl-thiophene, now known as the scintillator BBOT (Compound VIII), for example, is about 12 times more soluble in toluene than the unsubstituted compound.

Most of the spectra of the derivatives are similar in shape. Introduction of the alkyl-groups produces the expected bathochromic shifts in the spectra, as can be seen from the values of λ_{\max} .

TABLE Ia-- Derivatives from the Benzoxazolyl-Thiophene Series

No.	Compound	Formula	Solubility in toluene at 20°C (g/l)	mp (°C)	Spectrum of absorption* λ_{max} (nm)	Spectrum of fl. in toluene $\epsilon \cdot 10^{-3}$ λ_{max} (nm)
I	2,5-Bis-benzoxazolyl(2')-thiophene		4.7	220	367 (D)	46.4 429
II	2,5-Bis-[5'-methylbenzoxazolyl(2')]-thiophene		2.8	219	375 (D)	50.4 435
III	2,5-Bis-[4', 5'-dimethylbenzoxazolyl(2')]-thiophene		0.05	287	383 (D)	48.5 436
IV	2,5-Bis-[4', 5'-dimethylbenzoxazolyl(2')]-3,4-dimethylthiophene		0.33	319	380 (D)	46.0 439
V	2,5-Bis-[5'-isopropylbenzoxazolyl(2')]-3,4-dimethylthiophene		11.7	181	375 (D)	44.2 436
VI	2-Benzoxazolyl(2')-5-[7'-sec-butyl-benzoxazolyl(2')]-thiophene		70.2	137	371 (D)	42.4 434
VII	2-Benzoxazolyl(2')-5-[5'-t-butyl-benzoxazolyl(2')]-thiophene		13.3	189	372 (D)	44.4 432
VIII	2,5-Bis-[5'-t-butylbenzoxazolyl(2')]-thiophene (BBOT)		58.8	202	372 (D)	48.8 435

* measured in (D) = dimethylformamide, (E) = ethanol, (Di) = dioxane.

TABLE 1 b— Derivatives from the 2-Phenylbenzoxazole Series

No.	Compound	Formula	Solubility in toluene at 20°C (g/l) $\frac{1}{100}$	mp (°C)	Spectrum of absorption*) λ_{max} (nm)	Spectrum of fl. in toluene λ_{max} (nm)
IX	2-Phenylbenzoxazole		329	103	301 (D)	348
X	2-(4'-Methylphenyl)- benzoxazole		165	118	305 (D)	356
XI	2-(4'-Methylphenyl)-5- methylbenzoxazole		51	133	306 (Di)	360
XII	2-(4'-Methylphenyl)-5-t- butylbenzoxazole		214	113	307 (E)	361
XIII	2-(4'-t-Butylphenyl)- benzoxazole		426	105	303 (E)	362
XIV	2-Phenyl-5-t-butyl- benzoxazole		627	83	304 (E)	362
XV	2-(4'-t-Butylphenyl)-5-t- butylbenzoxazole		340	157	307 (E)	362
XVI	2-(4'-Biphenyl)-benzoxazole		78	138	316 (D)	363
XVII	2-(4'-Biphenyl)-5-t- butylbenzoxazole		181	135	320 (Di)	371
XVIII	2-(4'-Biphenyl)-6-phenyl- benzoxazole (PBBO)		4.2	190	331 (Di)	396

*)measured in (D) = dimethylformamide, (E) = ethanol, (Di) = dioxane.

TABLE 1c—Derivatives from the 1,3,4-Oxadiazole Series

No.	Compound	Formula	Solubility in toluene at 20°C (g/l)	mp (°C)	Spectrum of absorption*)		Spectrum of fl. in toluene $\lambda_{\max}(\text{nm})$
					$\lambda_{\max}(\text{nm})$	$\epsilon \cdot 10^{-3}$	
XIX	2,5-Diphenyl-1,3,4-oxadiazole (PPD)		79	139	281 (E)	26.6	360
XX	2-(4'-t-Butylphenyl)-5-phenyl-1,3,4-oxadiazole		294	99	288 (E)	30.4	360
XXI	2,5-Di-(4'-t-butylphenyl)-1,3,4-oxadiazole		559	136	293 (Di)	32.0	361
XXII	2-Phenyl-5-(4''-biphenyl)-1,3,4-oxadiazole (PBD)		13	169	303 (Di)	43.2	361
XXIII	2-(4'-t-Butylphenyl)-5-(4''-biphenyl)-1,3,4-oxadiazole (Butyl-PBD)		105	139	307 (Di)	43.8	366

* measured in (D) = dimethylformamide, (E) = ethanol, (Di) = dioxane.

In the Table 1b the properties of the derivatives of the 2-phenylbenzoxazole series are quoted. The behaviour of these compounds is very similar to these in Table 1a. Here again, the introduction of methyl groups lowers the solubility (cf. the compounds IX, X, XI or the two compounds XIV and XII). The solubility increases by introduction of tert-butyl groups (or other branched alkyl chains). The introduction of phenyl-groups lowers the solubility as expected. Because of the high solubility of the unsubstituted 2-phenylbenzoxazole, the solubility of the diphenyl-substituted compound still remains well over 4 g/l (Compound XVIII, PBBO). The bathochromatic shift due to the two phenyl groups is high, and the emission of PBBO matches very closely with the sensitivity optimum of the new photocathodes.

Finally, in Table 1c some of the tert-butyl substituted derivatives of the 1,3,4-oxadiazole series are summarized. Here the principle of solubilization by the introduction of tert-butyl groups can be applied to a compound known as one of the best primary solutes, the PBD (compound XXII). Because of its poor solubility PBD has found only a very limited application. Butyl-PBD (compound XXIII) is about 8 times more soluble than the unsubstituted PBD. The introduction of tert-butyl affects the high photon yield of PBD in a negligible manner as will be shown later. Although a bathochromic shift of λ_{max} is observed the shape of the emission spectrum of PBD is influenced by the tert-butyl group in such a manner, that the mean wavelength of emission of Butyl-PBD lies somewhat below that of unsubstituted PBD.

3. Scintillation Properties

Photon yield

It has been common practice to use the RPH (relative pulse height, normalized to unity for 3 g/l PPO in toluene) as an index for the light yield of a given scintillator. Because of the dependence of RPH on the spectral effects, the value of RPH fails to give evidence about the performance of various compounds as sole solutes in assemblies with different "optics" (reflectors, vials, photocathode types), or when used as primary solutes in ternary systems. The proper index for the comparison of scintillator solutes is the relativ photon yield (RPY) as defined by Swank⁸. However, the experimental method for the deter-

mination of RPY given by Swank is rather troublesome. Therefore, we have tried to get some estimates for RPY from interrelated measurements on one solute with different photomultipliers and different secondary solutes used. The data obtained on RPY are claimed to be correct within $\pm 5\%$.

In Table 2 the RPH values and the RPY estimates of some selected compounds from the benzoxazolyl-thiophene, phenylbenzoxazole and oxadiazole series are given. The RPH values were measured in binary systems with the actual compound as sole solute, and in ternary systems with Dimethyl-POPOP and PBBO added as wavelength shifters. The counter used employs an aluminium reflector, a quartz vial and a Philips photomultiplier 56 AVP, the POPOP/TP ratio of the whole assembly was 1.30. All solutions were air-saturated.

As can be seen, Butyl-PBD exhibits a relative photon yield lower by only about 5% than PBD. The RPH of 1.15 for Butyl-PBD, as compared with the value of 1.30 for unsubstituted PBD, is due to the combination of slightly lower photon yield and light emission at shorter wavelength by the former compound. Measurements in assemblies with lower POPOP/TP ratio (i.e. in counters with modern photomultipliers with photo-

TABLE 2 — Scintillation properties of some selected compounds quoted in Table 1

Compound		as sole solute at c_0 in toluene	as primary solute at 5 g/l in toluene with 0.5 g/l secondary added:		Relative photon yield	
			Dimethyl- POPOP	PBBO		
No.	Abbreviation	c_0 (g/l)	RPH	RPH	RPH	RPY
	p-TP	8 ^s	0.98	1.23	1.33	1.30
	PPO	4	1.01	1.03	1.07	1.00
VIII	BBOT	6	1.08	—	—	1.00 — 1.05
XIII		6	0.91	1.14	1.21	1.15
XIV		6	0.79	1.02	1.09	1.00
XV		7	0.88	1.09	1.14	1.10
XVII		4	0.90	1.15	1.10	1.10
XVIII	PBBO	4 ^s	1.25	—	—	1.25
XXI	Dibutyl-PPD	5	1.03	1.17	1.23	1.20
XXII	PBD	10	1.30	1.18	1.23	1.25 — 1.30
XXIII	Butyl-PBD	7	1.15	1.24	1.27	1.20 — 1.25

cathode sensitivity extended to shorter wavelength) yield approximately the same RPH values for both solutes.† Although unsubstituted PBD does not yield useful ternary systems with most of the known secondaries, Butyl-PBD does so. This can be of great importance in large volume applications (e.g. in whole body counting), where a wavelength shifter is necessary because of the selfabsorption of the radiation by the primary solute, or in plastic scintillators.

Among the benzoxazole derivatives there are some highly soluble potential scintillator solutes with RPY values of up to 15% higher than that of the standard PPO. The most useful compound of this series is PBBO, which can be used as a very efficient wavelength shifter. With the exception of compound XVII, in all the measured ternary systems we obtained higher RPH values with PBBO than with the standard secondary solute Dimethyl-POPOP.

Up to date there are no exact measurements on the fluorescence decay times of the quoted new solutes. Preliminary observations with the aid of the ultrafast RCA photomultiplier C 70045 A and a sampling oscilloscope indicate the decay times to be slightly below or in the order of 1 nsec. Accurate data will be published later.

Photochemical degradation

It is well known that many fluorescing compounds undergo rapid photochemical degradation when irradiated by ultraviolet and visible light. We have found the solutions of the compounds of the benzoxazole, benzoxazolyl-thiophene and of the 1,3,4-oxadiazole series to be of remarkable stability to light exposure.

In Fig. 1 the results of investigations on photochemical stability of the standard compounds PPO, POPOP and Dimethyl-POPOP and the new solutes BBOT, PBBO and Butyl-PBD are plotted. Toluene solutions of these compounds, at a concentration of 0.5 g/l, were irradiated by a Xenon lamp at an intensity of about 180,000 lux. The absorbance of the solution at the maximum of the ultraviolet absorption was measured periodically. The reduction of absorbance has been taken as a measure for the degree of the radiation damage. As it can be seen from Fig. 1, PPO, POPOP and Dimethyl-POPOP are quite sensitive to light exposure in toluene solution, whereas BBOT, PBBO and Butyl-

† More detailed data to be published⁹.

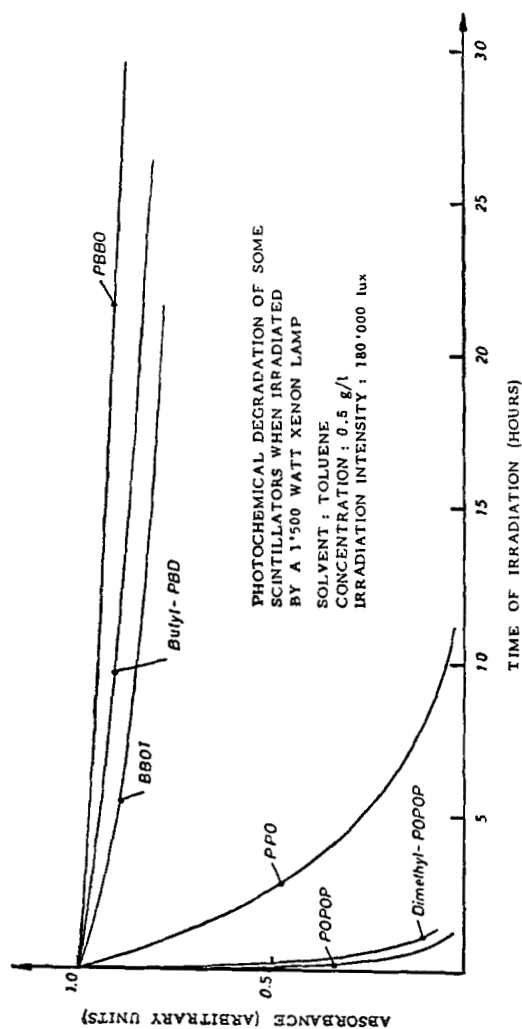


Figure 1. Photochemical degradation of some scintillators. The air-saturated solutions of the scintillator compounds in toluene were irradiated by a Xenon lamp, the reduction of absorbance has been taken as a measure for the degree of the radiation damage.

PBD remain almost unaltered by the irradiation. Due to its high photochemical stability, and some other special features, BBOT has been chosen by Berlman¹⁰ as the standard scintillator in his recent studies on the fluorescence spectra of aromatic compounds.

The photochemical stability of PBBO and Butyl-PBD is so high that the solutions of these compounds could be used by Siegenthaler and Weber¹¹ for shifting the intense light for optical pumping of lasers to proper wavelength regions.

Effects of quenching agents

The counting efficiency of β emitting isotopes in liquid scintillators is known¹² to be approximately an exponential function of the concentration of an added chemical quenching agent. In Fig. 2 the C^{14} counting efficiencies in various scintillators for different concentrations of a representative quenching agent (CCl_4) are plotted. A half-value concen-

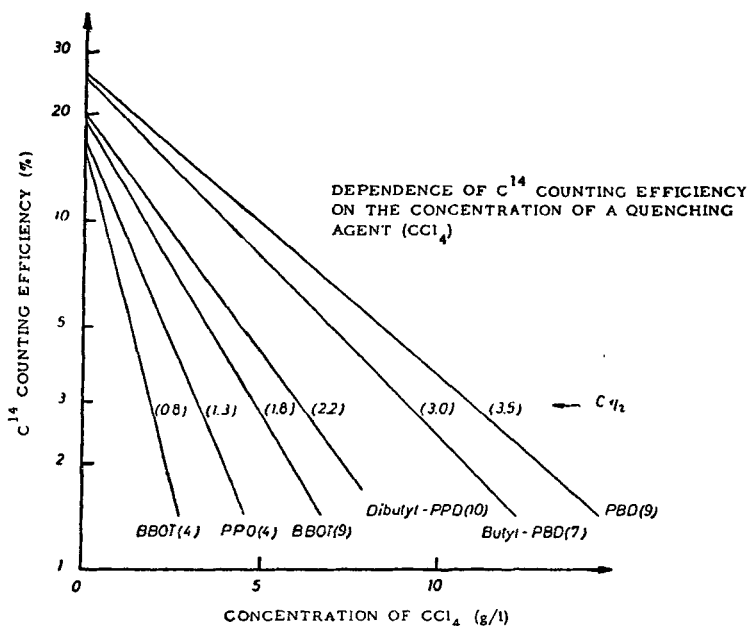


Figure 2. Dependence of C^{14} counting efficiency on the concentration of CCl_4 . The actual concentrations of the solutes in toluene are quoted in brackets. $c_{1/2}$ denotes the so called half-value concentration for which the initial counting efficiency is diminished by a factor of 2.

tration $c_{1/2}$ can be defined for which the initial counting efficiency is diminished by a factor of 2. The $c_{1/2}$ -values for each scintillator in Fig. 2 are quoted in brackets.

Similar to PBD, Butyl-PBD at the optimum concentration (7 g/l) exhibits very good resistance to quenching effects, as indicated by the high value of $c_{1/2}$. A high insensitivity of Butyl-PBD to chemical, as well as to the color quenching, has been recently reported by Scales.¹³

4. Conclusions

The results presented can be summarized as follows: By the introduction of branched alkyl groups, especially of the tet-butyl group, the solubilities of the benzoxazolyl-thiophene, phenylbenzoxazole and 1,3,4-oxadiazole derivatives in toluene can be increased. Among the new compounds there are some highly efficient scintillation solutes,[†] especially with regard to the practical aspects.

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[†] BBOT, Butyl-PBD and PBBO are now commercially available.