PMP, A NOVEL SOLUTE FOR LIQUID AND PLASTIC SCINTILLATION COUNTING

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ABSTRACT

The excellent fluorescence properties of PMP (1-phenyl-3-mesityl-2-pyrazoline) such as long wavelength emission of over 400 nm, and high fluorescence quantum yield with a short decay time together with a great solubility of more than one Mol/L in toluene make this compound a promising solute for scintillation counting. The Stokes' shift of PMP of over 10,000 cm^{-1} is twice as large as that of the commonly used PPO. Due to this unusually large Stokes' shift PMP can be used as a primary solute without requiring a secondary solute as wavelength shifter. A comparison of the scintillation properties of PMP and PPO in toluene reveals that the counting efficiency for ^{14}C is better for PMP while the ^{3}H efficiency is equally good. Due to the large Stokes' shift, PMP is about 50% less sensitive to color quenching than PPO. Compared to the solute combinations PPO/secondary solutes, the scintillation counting efficiency of PMP for ^{14}C in toluene or xylene is the same, while the absolute ^{3}H efficiency of PPO/secondary solutes in cocktails with emulsifiers is about 10% higher. The PMP scintillation efficiency for ^{14}C as well as ^{3}H in chemical quenching by urine is more or less the same as for PPO/dimethyl-POPOP. PMP is more sensitive to quenching by halogenated solvents. In the dioxane-based scintillation, this sensitivity to chemical quenching by $CHCl_3$ vanishes and the counting efficiencies for ^{14}C and ^{3}H are as good as for PPO/dimethyl-POPOP or PPO/bis-MSB. Due to the large Stokes' shift, the self-absorption of the scintillation light by PMP is lower than in conventional scintillators. This offers good possibilities in very large-volume applications of liquid as well as plastic scintillators.

INTRODUCTION

Some thirty years ago, 2,5-diphenyloxazole (PPO) was recognized by Hayes[1] as one of the best organic scintillators. Though hundreds of organic compounds have since been evaluated as solutes, PPO is still the most popular primary organic scintillator. We have recently shown that the class of 1,3-diphenyl-2-pyrazolines exhibits unusually large Stokes' shifts when properly substituted by methyl and/or methoxy substituents in the ortho, ortho' positions of the phenyl rings[2,3]. These sterically hindered 1,3-diphenyl-2-pyrazolines have a promising potential as novel primary solutes for liquid scintillation counting[3,4]. This paper summarizes the results of a screening program on the application of 1-phenyl-3-mesityl-2-pyrazoline, henceforth called PMP, as a novel solute for scintillation counting in comparison to the commonly used PPO.

EXPERIMENTAL

The absolute fluorescence spectra, fluorescence quantum yields and fluorescence decay times were determined on a self-constructed spectrofluorimeter and a fluorimeter using the pulse sampling method. Details about the instrumentation and the measurement technique have been published earlier[2,5]. Scintillation counting was performed at room temperature in our laboratory using a Packard Tri-Carb liquid scintillation spectrometer, Model 2420. Some screening results, especially on quenching, have been obtained in other laboratories which are indicated in the acknowledgement. They used the models 3380 and 460 CD of the same company. In all measurements 10 ml scintillator volume in regular glass or plastic vials have been used with standard ^{14}C or ^{3}H solutions added with a Hamilton syringe. The composition of the dioxane scintillator was 7 g PPO, 0.3 g dimethyl-POPOP and 100 g naphthalene per liter of dioxane. In comparison with PPO (5 g/l) 5 grams per liter of PMP were dissolved inthe appropriate scintillator solvent investigated. The scintillator composition PPO/bis-MSB was 7 g PPO and 1.25 g bis-MSB per liter of toluene, for the combination of PPO/dimethyl-POPOP the commercial solution Omni-Szintisol (Merck, Darmstadt) was used. All chemicals were of

scintillation grade and to exclude any doubt the same chemicals and solvents were used for the comparison of PPO and PMP. PMP was synthesized with an 85% yield by condensation of mesityl vinyl ketone with phenyl hydrazine and recrystallization from cyclohexane. PMP, mp 96°C (λ_{max} 292.5 nm, ε 2.03 x 10^4 l . $M^{-1}cm^{-1}$ in cyclohexane) is a stable white crystalline compound.

RESULTS AND DISCUSSION

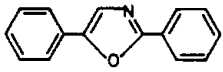
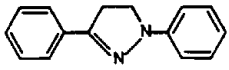
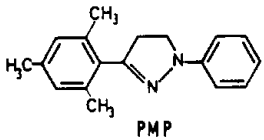
Photophysical Properties

Several photophysical properties of a fluorescent organic compound must be considered when it is used as a solute for scintillation counting. The fluorescence or photon yield of the scintillator must be high and the fluorescence decay time should be short. Spectral matching of the scintillator emission spectrum with the spectral sensitivity of the photocathode of the common multipliers must be sufficient. These requirements are imposed because of the very poor absolute scintillation efficiency of organic scintillators of the order of 1.5 - 21.5%[7]. Besides these photophysical properties, the solubility in the solvent used should be high and, for practical applications, the scintillator should be as little affected by quenching agents as possible.

The main photophysical properties of PPO, of 1,3-diphenyl-2-pyrazoline (DP) - the parent compound of PMP - and of PMP in benzene are compiled in Table 1. The fluorescence quantum yield, Q, of DP and PMP is slightly higher than that of PPO while the fluorescence decay time, τ, of PPO is shorter.

Unlike in PPO, there is no "normal" π-electron conjugation in DP. The excellent fluorescence properties of DP are linked to the conjugation of the π-systems of the phenyl rings via the lone pair electron of the N-phenyl nitrogen atom. Especially in the first excited singlet state this conjugation is favored due to an intra-molecular charge transfer of the π-π^* state, which gives rise to a much larger dipole moment in the excited singlet state as compared to the ground state[2,8]. The only advantage of DP over PPO is the maximum of the fluorescence spectrum, λ_F, which is red shifted by 80 nm, thus enabling a better matching of scintillation with the spectral

Table 1. Photophysical Properties of PPO, DP and PMP in Benzene at Room Temperature.

Scintillator	S[g/l][a]	Q[b]	τ[n sec][b]	λ_F[nm]	ΔSt.10^3[cm^{-1}]
 PPO	414	0.79	1.3	365	5.24
 DP	49	0.92	3.2	444	4.98
 PMP	335	0.88	3.0	425	10.37

a) in toluene at 20°C
b) in degassed solutions

sensitivity of the photocathode of common photomultipliers. The solubility, S, of DP is poor compared to PPO. PMP, however, combines very good photophysical properties such as high fluorescence quantum yield, a short decay time and the long wavelength emission of the fluorescence maximum with a much higher solubility (see Table 1). The most striking difference of PMP in comparison to PPO and DP is the unusually large Stokes' shift, ΔSt, of more than 10,000 cm^{-1}. Since there is no fine structure in the absorption and fluorescence spectrum at room temperature, the 0-0 transition is difficult to determine and the energy difference of the absorption and emission maxima is therefore taken as a measure of the Stokes' shift. Obviously, in the first excited singlet state PMP is planar due to an intramolecular charge transfer after π-π* excitation like in DP[2]. Sterical hindrance by the bulky methyl groups in the 2,6-position results in a large hyposchromic shift of the absorption spectrum of PMP compared to DP while the fluorescence spectrum remains nearly unaffected

energetically[2,3]. Due to the unusually large Stokes' shift, the sterically hindered PMP can be used as a primary solute and no secondary solute is required. Among the sterically hindred 1,3-diphenyl-2-pyrazolines tested for liquid scintillation counting[4], PMP is a compromise in terms of photophysical and scintillation properties and easy access to synthesis[9].

SCINTILLATION PROPERTIES

Comparison of the scintillation characteristics of PMP with the commonly used PPO in toluene or xylene reveals:

1. The maximum of the scintillation light of PMP is red shifted by about 60 nm (see Table 1).
2. The Stokes' shift of PMP is twice as large as that of PPO (see Table 1).
3. The counting efficiency of PMP for ^{14}C is better by 5%.
4. The counting efficiency for ^{3}H of both solutes is equally effective with 48% measured in a Tri-Carb 3380.
5. The maximum counting efficiency of both solutes is about 5 g/l.
6. PMP is about 50% less sensitive to color quenching, based on the addition of 1 ml 2,4-dinitrophenyl hydrazine in ethanol (see Table 2).

It is interesting that the concentration dependence of the scintillation efficiency of PMP for ^{14}C as well as for ^{3}H in toluene at room temperature shows a very shallow maximum between 0.01 and 0.1 molar solutions[4]. Because of the very large Stokes' shift self-absorption of the scintillation light is very low. Even in a one-molar solution nearly the same counting efficiency for ^{14}C toluene is obtained as in a 0.01 M solution, a very unusual feature for a primary solute. This indicates that there is little tendency towards self-quenching in PMP.

Since, however, PMP scintillates in the range of 400 - 450 nm, we compared the counting efficiency of PMP with those of the combination of PPO and two commonly used secondary solutes such as POPOP or bis-MSB, in order to match the short-wavelength scintillation of PPO with

the same spectral range of PMP. Comparison of the counting efficiency of PMP with the scintillator combinations PPO/dimethyl-POPOP and PPO/bis-MSB for ^{14}C and ^{3}H reveals that in unquenched solutions of toluene PMP is as effective as both combinations of PPO with secondary solutes. In cocktails of toluene with 40% emulsifier the absolute tritium efficiency is equal for PMP and PPO, dependent on amounts of water added while the combination PPO/bis-MSB shows a better ^{3}H efficiency of about 10%.

In color quenching by 2,4-dinitrophenyl hydrazine in ethanol PMP is superior to all tested combinations of PPO containing secondary solutes.

Table 2. Color Quenching (AES Ratios) of Scintillators with ^{3}H Excitation in Toluene as a Function of Added Amounts of 2,4-Dinitrophenyl Hydrazine in Ethanol (in ml). Automatic External Standard (AES) Ratios Measured in a Tri-Carb 3380 are Given.

Scintillator	Volume of 2,4-Dinitrophenyl Hydrazine Solution none	0.4 ml	1.0 ml
PMP	9.06	6.85	5.56
PPO	8.90	4.56	2.43
PPO/bis-MSB	9.50	6.99	5.48
PPO/POPOP	9.30	6.50	4.95

The scintillation efficiency in chemical quenching by urine (up to 20%) for ^{14}C as well as for ^{3}H is more or less the same in xylene or in the dioxane scintillator (see Fig. 1).

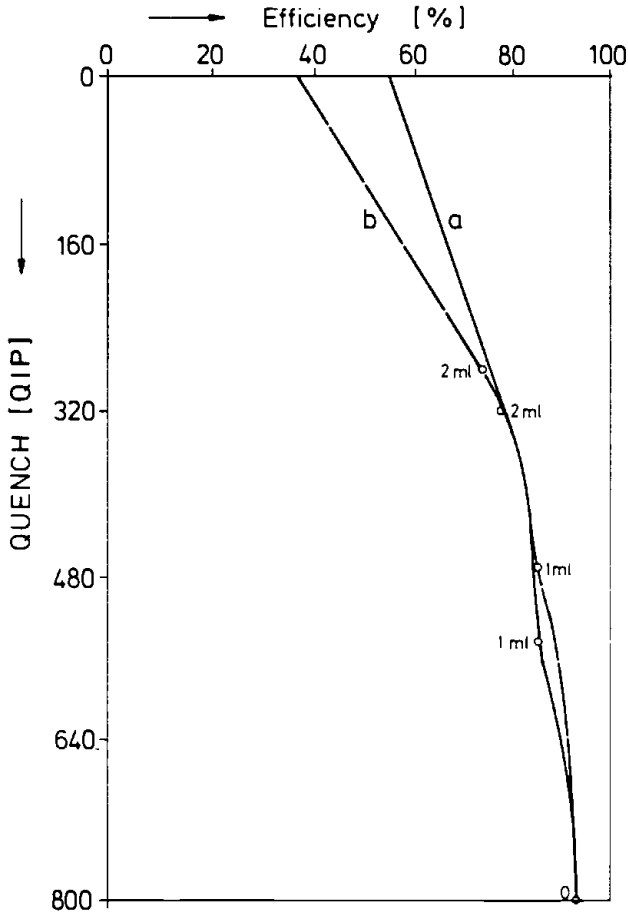


Figure 1. Chemical quenching of PPO (curve a) and PMP (curve b) in the dioxane scintillator as a function of added ml of urine. ^{14}C dpm: 17,400.

The counting efficiency of β-emitting nuclides in liquid scintillators is known to be approximately an exponential function of the concentration of the chemical quencher added[10]. In this respect, PMP is more sensitive to chemical quenching by halogenated solvents (CCl_4, $CHCl_3$) in ^{14}C as well as ^{3}H counting, than PPO with bis-MSB or dimethyl-POPOP as secondary solute in toluene or xylene. While, for

example, 5% $CHCl_3$ reduces by 26% the ^{14}C counting efficiency of PPO/dimethyl-POPOP, the PMP counting efficiency is reduced by 54% compared to the unquenched solution. $CHCl_3$ 10% reduces by 40% and 95%, respectively, the ^{14}C counting efficiency of both scintillators. The greater PMP sensitivity to quenching by halogenated solvents is due to the fact that the first excited singlet state of PMP undergoes a photochemical reaction with CCl_4 and $CHCl_3$[11]. It is in line with these findings that DP and PMP do not fluoresce in CCl_4 and $CHCl_3$. It is interesting that the greater sensitivity of PMP to quenching by halogenated solvents does not exist in the dioxane scintillator. PMP and PPO/dimethyl-POPOP in the dioxane scintillator do not show differences in the quenching behavior with increasing amounts of $CHCl_3$ added under ^{14}C as well as ^{3}H excitation.

Due to the large Stokes' shift, the self-absorption by PMP of its own scintillation light is lower than in conventional scintillators. This can be of great importance in large-volume applications such as in whole-body counters or very large plastic scintillators. Since the intensity of the transmitted photons is related to the solute concentration and the length of the solution through which the photon has to travel to the photomultiplier, the light attenuation length of PMP with its large Stokes' shift and its low tendency to self-quenching should be better than that of other commonly used solutes in large-volume counting. In this respect, the solubility of PMP in mineral oil is very good and allows preparation of nearly 0.1 M solution at room temperature. Mineral oils are often used in whole-body scintillation counting because of their high flash points, low toxicity and low cost. Polymethyl methacrylate (PMMA) is a favorite polymer for very large plastic scintillators. Important properties of a good plastic scintillator are the light output, the decay time and the attenuation length. The fluorescence maximum of PMP in PMMA lies at 420 nm, the fluorescence quantum yield is 0.61 and the fluorescence decay time is 2.5 nanoseconds[12]. Thus, PMP provides also a promising potential as solute in plastic scintillation counting. Results on other plastic scintillation properties with PMP as solute will be reported elsewhere.

CONCLUSION

A comparison of the scintillation counting properties of PMP with PPO reveals that PMP is superior to PPO and can be used as primary solute without requiring a secondary solute. Compared to commonly used solute combinations of PPO/secondary solutes, the scintillation properties of PMP are equally good except for ^{3}H counting in cocktails with water. Due to the very large Stokes' shift PMP is less sensitive to color quenching than other organic scintillators. PMP offers promising potential as solute in liquid and plastic large-volume scintillation counters.

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