

PROGRESS IN THE DEVELOPMENT OF WATER-MISCIBLE
NON-HAZARDOUS LIQUID SCINTILLATION SOLVENTS

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ABSTRACT

Liquid scintillation counting (LSC) of aqueous samples presents problems of immiscibility between the water which is the solvent of the labelled molecules and the hydrophobic LSC solvents such as toluene and xylene. A water miscible LSC solvent would solve many problems of sample preparation currently encountered. We have previously reported such a solvent¹. This paper reports studies directed toward improving the ³H counting efficiency and fluidity of water miscible LSC solvents.

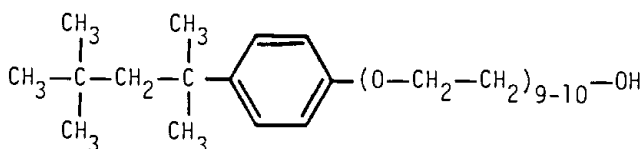
Experiments with model compounds have shown that improved water miscible LSC solvents can be developed with fluidity up to 50% v/v added water. The length of the polyethylene chain is not critical beyond that needed to confer water miscibility. Relative scintillation yield studies indicate that termination of the polyethylene glycol chain of these water miscible LSC solvents with an ether group instead of a hydroxyl group should significantly increase ³H counting efficiency.

INTRODUCTION

We have previously shown¹ that the detergent Triton X-100 can function as a scintillation solvent and when combined with appropriate primary and secondary fluors will form a water miscible liquid scintillation cocktail. This cocktail has the following advantages: (1) it is water miscible at concentrations up to 60%; (2) it has a flash point of over 300°F, (low flammability); (3) it has no organic solvent fumes and has low toxicity; and (4) it is a non-hazardous waste according to the EPA. This last point is a significant

administrative and financial advantage.

This cocktail has two disadvantages. (1) The tritium counting efficiency is only 17%, and (2) it forms gels at higher levels of water addition. Examination of the structure of Triton X-100 reveals that it is composed of a hydrophobic isooctyl group, a central aromatic ring, and a polyethylene glycol chain 9-10 oxyethylene monomers long in a paraposition to the isooctyl group.



As a scintillation solvent for aqueous samples, the hydrophobic group may not be needed. If a new solvent were synthesized without the large hydrophobic group, a small polyethylene glycol group may be able to provide adequate water miscibility. This smaller molecule would increase the relative molar concentration of the aromatic group which is the probable scintillating portion of the molecule (since most other scintillators are alkyl aromatic compounds). This should result in higher scintillation yield and, therefore, higher ^3H counting efficiency. This paper reports results of experiments exploring the above hypothesis with model compounds.

EXPERIMENTAL

Absorption spectra were obtained using a Perkin-Elmer model 552 recording spectrophotometer. The effect of various compounds on relative scintillation yield was measured by a modification of the method of Hayes² et al. A toluene PPO, bis-MSB cocktail was used as a standard and the effect of replacing toluene with other chemicals on the scintillation yield was measured. The PPO and bis-MSB concentrations were constant in all samples.

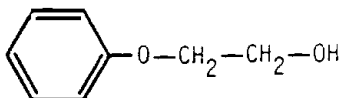
A transparent lucite solid plastic mini-vial holder with the external dimensions (2.5 cm) of a standard 20 ml scintillation vial

and cylindrical hole in its center to hold a 7 ml glass mini-vial was utilized. A 2.5 cm diameter plastic encapsulated ^{137}Cs source was taped to the bottom of the mini-vial holder. Five ml volumes of samples to be measured were precisely pipetted into glass mini-vials and placed in the holder above the ^{137}Cs source. Care was taken to assure that the volumes added were identical because the accuracy of this system is volume dependent.

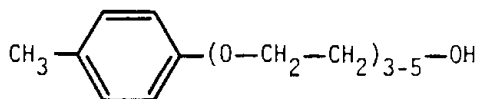
The assembly was placed into a Packard 3255 liquid scintillation counter and lowered by the sample elevator into counting position. The Model 3255 counter comes equipped with a multichannel analyzer (MCA) output which is connected to the output of the summing amplifier. The signal was shaped and amplified 32X by a Canberra model 814 PAD and was fed to a Tracor Northern TN 1705 MCA. The MCA upper discriminator was set to maximum and the lower discriminator set to 8/1000 to eliminate noise. The conversion gain was 1024 (the same as the number of channels in the MCA). The horizontal scale expansion was maximum. These settings gave a Compton spectrum from the ^{137}Cs source with 8g/L of PPO and 0.5 g/l bis-MSB in toluene utilizing 734 of the 1024 channels. The Compton spectra were acquired until the top of the Compton edge reached 1000 counts per channel and the elapsed live time recorded. The mini-vial was removed and a background spectrum from the mini-vial holder, empty mini-vial, and ^{137}Cs source was counted for the same live time in the subtraction mode. The inflection point on the Compton edge was determined by the method of Horrocks³ and the MCA channel corresponding to that point was recorded as the scintillation yield for that sample.

RESULTS

Evaluation of 2 phenoxy ethanol (2PE) as a LSC solvent revealed that it would accept no more than 12% v/v water addition before becoming biphasic. With no water addition its tritium counting efficiency was 27%.



A proprietary LSC cocktail Safety Scintillation Cocktail 1 provided by the Sagami Chemical Research Center was also evaluated. This cocktail is based on their patent⁴. The structure published in the patent is shown below.



This cocktail has a tritium counting efficiency of 15% and was miscible with up to 45% v/v added water.

The low tritium counting efficiency with these substances as well as with Triton X-100 suggested that color quenching might be occurring, consequently their U.V. spectra were taken. All three substances had significant absorption at the wavelengths of emission of PPO. The addition of the secondary fluor bis-MSB increased ³H counting efficiency by 20% in all three cocktails.

The possibility of chemical self-quenching by these LSC solvents was further tested by determining the scintillation yield as a function of the concentration of various functional groups.

Table 1. Effect of number of ethylene glycol groups on relative scintillation yield

$\text{CH}_3\text{-O-(CH}_2\text{-CH}_2\text{-O-)}_X\text{CH}_3$				
% substance in toluene cocktail	number of ethylene glycol groups (X)			
	1	2	3	4
	relative scintillation yield			
0	100	100	100	100
25	87	97	100	99
50	52	88	80	80
75	19	56	44	47
100	0	29	20	22

Table 1 shows the relative scintillation yield when the number of ethylene glycol groups in polyethylene glycol dimethyl ether was varied. As can be seen in Table 1, increasing the number of ethylene glycol groups beyond three does not cause a significant additional decrease in scintillation yield.

The functional group terminating the polyethylene glycol chain has a major effect on scintillation yield. Table 2 shows the relative effect of diethyl ether, ethyl acetate, or ethanol on scintillation yield. The more polar the functional group the lower the scintillation yield.

Table 2. Effect of ethers, esters or alcohols on relative scintillation yield

% substance in toluene cocktail	Relative scintillation yield		
	diethyl ether	ethyl acetate	ethyl alcohol
0	100	100	100
25	88	92	58
50	80	68	31
75	57	42	17
100	13	-	-

Since the polyethylene glycol substituted aromatic LSC solvents tested above all have their PEG chains terminated with alcohol groups the effect of PEG with ether and/or alcohol terminating groups on scintillation yield was tested (Table 3).

Various ethylene glycols with monomethyl, dimethyl, mono ethyl and diethyl ether terminating groups were evaluated. The data obtained formed two groups. All PEG compounds which were terminated at both ends of the chain as ethers (methyl or ethyl) had a minimum effect on scintillation yield. The presence of a hydroxyl group on the PEG cut the scintillation yield drastically compared to the diethers which had no hydroxyl groups.

Table 3. Relative scintillation yield of PEG diethers vs mono ether, mono hydroxy compounds

Percent substance in toluene cocktail	Relative scintillation yield	
	ethylene glycol diether	ethylene glycol mono ether, mono hydroxy
	$\text{CH}_3-(\text{O}-\text{CH}_2-\text{CH}_2)_x-\text{O}-\text{CH}_3$	$\text{CH}_3-(\text{O}-\text{CH}_2-\text{CH}_2)_x-\text{OH}$
0	100	100
25	100	80
50	84	47
75	51	19
100	24	2

The data in Table 3 show that PEG diethers will themselves scintillate with a relative scintillation yield of 24. PEG mono ether, mono hydroxy compounds have a relative scintillation yield less than 1/10 as high. In mixtures with toluene the hydroxyl group clearly suppresses scintillation yield. It seems probable that water miscible scintillation cocktails such as those reported above would have significantly higher scintillation yields (and therefore higher ^3H counting efficiencies) if the free hydroxyl group on the end of the polyethylene glycol chain were converted to an ether group. The effect of this on the water miscibility of the cocktail is unknown at this time, however, tri and tetra polyethylene glycol diethers are themselves water miscible.

CONCLUSIONS

Studies have shown that the development of water miscible non-gelling LSC cocktails is possible. The cocktails studied thus far all have the shortcoming of a relatively low ^3H counting efficiency (= 15%). We have shown that addition of the secondary fluor bis-MSB increases ^3H counting efficiency by 20%.

The length of the polyethylene chain does not seem to affect

scintillation yield. However, the termination of the polyethylene chain with a hydroxyl group causes a significantly lower scintillation yield than the termination with an ether group. In previous studies, increases in scintillation yield were proportional to increases in ^3H counting efficiency. These studies indicate that an aromatic group bonded to a polyethylene chain three to five ethylene glycol monomers long and terminated with an ether group may combine the desirable features of water miscibility, fluidity, low flammability, non toxicity, and a high ^3H counting efficiency.

REFERENCES

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