

SURFACTANTS BEHAVE AS SCINTILLATORS IN  
LIQUID SCINTILLATION COUNTING

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A number of solubilizers, proprietary mixtures of non-ionic and ionic surfactants have been used to make samples in aqueous solutions miscible with toluene, the organic solvent usually employed in liquid scintillation counting. We have discovered that such surfactants may increase the scintillation yield of quenched samples emitting sufficiently energetic photons, and may themselves act as efficient scintillators. Data on Biosolv-BBS-3 (distributed by Beckman Instruments, Inc.) are in press at the time of this writing (1). A detailed examination of our own series of surfactant combinations of known composition is in preparation (2). For this paper, we have selected our N-5 solubilizer, one with surfactant and scintillant properties very similar to those of the commercial BBS-3 preparation to illustrate the behavior of many surfactants, and the practical implications for liquid scintillation counting.

Materials and Methods

All samples were counted (except for reference standards) in aqueous solution and were air-equilibrated.

| Compounds        | Isotope          | Principal Emission On Decay | $E_{\max}$ (keV) | Activity (approx.) (DPM) |
|------------------|------------------|-----------------------------|------------------|--------------------------|
| H <sub>2</sub> O | <sup>3</sup> H   | β                           | 18               | 220,000                  |
| Cytosine         | <sup>14</sup> C  | β                           | 156              | 55,000                   |
| Insulin          | <sup>125</sup> I | γ<br>k-X-ray                | 35<br>27         | 362,000                  |
| NaI              | <sup>131</sup> I | γ<br>β                      | 360<br>610       | 420,000                  |

Table 1. Samples counted.

The absolute radioactivity of each sample was determined by comparing external standard channels ratios obtained with a Beckman LS-150 system to known quench correction curves. N-5 Solubilizer was mixed in our laboratory using commercially available nonyl-phenoxyethanol (94%) and sodium dihexylsulfosuccinate (6%). Spectra were obtained using a Nuclear Chicago 4096 Multi-channel analyzer interfaced to a Nuclear Chicago Mark II Liquid Scintillation System. The interface was set at analyzer Channel A and the attenuator at 0. Standard  $^3\text{H}$  settings were used to count  $^3\text{H}$  samples and  $^{125}\text{I}$  samples and  $^{14}\text{C}$  settings were used to count  $^{14}\text{C}$  and  $^{131}\text{I}$  with the upper discriminator set to infinity. After raw data were obtained, they were stored in the analyzer memory and the integral obtained and displayed. The resulting plots of spectral shape also indicate relative detection efficiency of identical amounts of radioactivity counted under different conditions: The greater the efficiency, the higher the curve will intersect the ordinate (counts per channel).

### RESULTS AND DISCUSSION

Figure 1 (a reproduction of Figure 2 in reference 1) shows that BBS-3 can serve as an efficient primary scintillator with  $\beta$ s above 100 keV maximum energy ( $E_{\text{max}}$ ). The emission spectrum of the fluorescence from BBS-3 is similar to those of the scintillators in general use (1). The higher excitation threshold is a handicap however, particularly with samples which are appreciably quenched; detection efficiency drops precipitously as the photoelectron spectrum shifts below 100 keV.

The effects of N-5 solubilizer on the spectrum of  $^3\text{H}$ , shown in figure 2 are therefore anticipated: N5 acts as a quencher, shifting the spectrum toward the low energy channels and decreasing efficiency with  $^3\text{H}$  samples. Therefore, a standard quench correction curve will indicate the loss of counting efficiency. (1).

Figure 3 illustrates the prediction that with more energetic  $\beta$ s, a surfactant will act as a scintillator even in the presence of a more efficient primary scintillator such as PPO.

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From the loss of efficiency indicated by the lower ordinate heights integral plots N5 did act as an impurity quencher. The raw spectral data show that there was a loss (as expected) of low energy photons when N-5 was added to a toluene PPO solution. It appears that there was a significant shift of the fluorescence spectrum toward higher energies.

The effect of this phenomenon on  $^{14}\text{C}$  quench correction is shown in Figure 4. If samples are being counted in a solution containing surfactant, it is therefore necessary to set up a quench correction curve with standards containing a similar amount of surfactant. Otherwise the radioactivity of quenched samples will be overestimated. A solution of 10% N-5 in toluene may be a practical "cocktail" for  $^{14}\text{C}$  counting, since the counting efficiency of the air-equilibrated sample shown in Figure 3 was 51% (28,000 DPM) vs. 80% for the N5-PPO, 7g/L sample (44,000 DPM).

The behavior of surfactants as scintillators for counting iodine isotopes has been of more than idle interest as our other paper in this volume (3) and elsewhere (4) testify.  $^{125}\text{I}$  is counted at good efficiency in 10% N5 solution (66%), slightly less than the 73% with a comparable solution of 10% BBS-3 (4). The solubilizers act as quenchers as they do with  $^3\text{H}$ . There is no evidence of a significant scintillator effect of solubilizers in the presence of PPO.

Although the comparison of the counting efficiencies of toluene/N5 (6%) and toluene alone (< 1%) indicates that some of the Compton electrons from the  $^{125}\text{I}$   $\gamma$  or k-X-rays are energetic enough to excite the surfactants to fluorescence.

The spectra in figure 5 show that in the absence of PPO it is no longer possible to differentiate the photo-peaks resulting from the 35 keV  $\gamma$  and the 27 keV k-X-ray. We have not yet examined the effect of surfactants on  $^{125}\text{I}$  quench-correction curves.

$^{131}\text{I}$  is counted with good efficiency in Toluene 10% N5 or toluene - 10% BBS-3: at virtually 100% efficiency with PPO, and at 87-97% efficiency without PPO. The high energy  $\beta$  of  $^{32}\text{P}$  is counted with similar ease and resistance to quenching (See Figure 1). The broad spectra of  $^{131}\text{I}$  in Figure 6 are attributable to the broad Compton Spectrum of the 360 keV  $E_{\text{max}} \gamma$ . As with the  $^{14}\text{C}$  spectrum (Figure 3) the presence of solubilizer has shifted the spectrum toward the higher energy ranges: the low energy peak is less conspicuous and the integral is less hyperbolic and more linear.

Without PPO present, there is an accumulation of counts at the lower end of the spectrum (Figure 7) much as there was with  $^{14}\text{C}$  - but few counts have fallen below detection limits. Some of this shift is attributable to the Cerenkov effect (5) which allows  $^{131}\text{I}$  to be counted at high efficiency. The counting efficiency of  $^{131}\text{I}$  insulin in toluene alone which we obtained (45%) may be spuriously low, since we cannot be sure all of the sample was in solution.

### CONCLUSIONS

The use of nonionic-anionic surfactant combinations in liquid scintillation counting mixtures will render quench correction curves prepared with dissimilar standards invalid if the  $\beta$ s emitted are more energetic than  $^3\text{H}$ . High energy  $\beta$ s can be counted at high efficiency in a 10% solution of nonyl phenoxyethanol (94%) and sodium dihexyl-sulfosuccinate (6%) in toluene alone.

Further investigation of the structure - activity relationships of micelles of water and surfactants in scintillation solvents to fluorescence yield will we hope, result in a new and less expensive kind of scintillation "cocktail".

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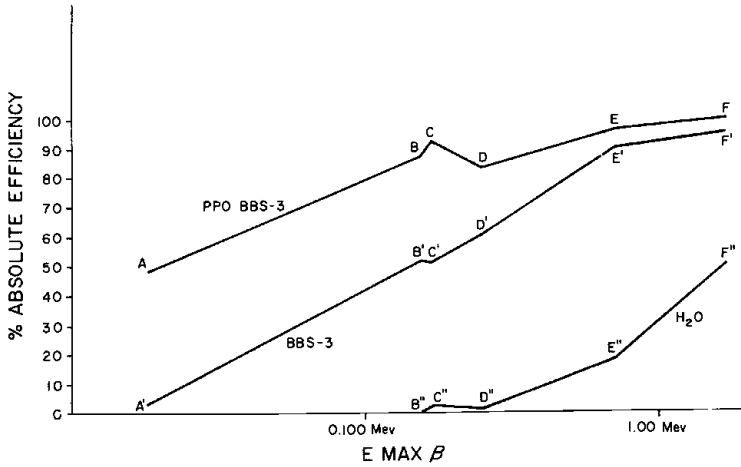


Figure 1. Relationship of detection efficiency to E max in various solutions of toluene-based  $\beta$ -emitting isotopes.

A.  $^3\text{H}$  B.  $^{14}\text{C}$  C.  $^{35}\text{S}$  D.  $^{45}\text{Ca}$  E.  $^{36}\text{Cl}$  F.  $^{32}\text{P}$

PPO-BBS: 7g PPO/L Toluene 90%: BBS-3 10%

BBS: toluene 90%: BBS-3 10%

H<sub>2</sub>O: This latter curve represents the Cerenkov efficiency of these isotopes in a system without anomalous refractive dispersion. (from Reference 1).

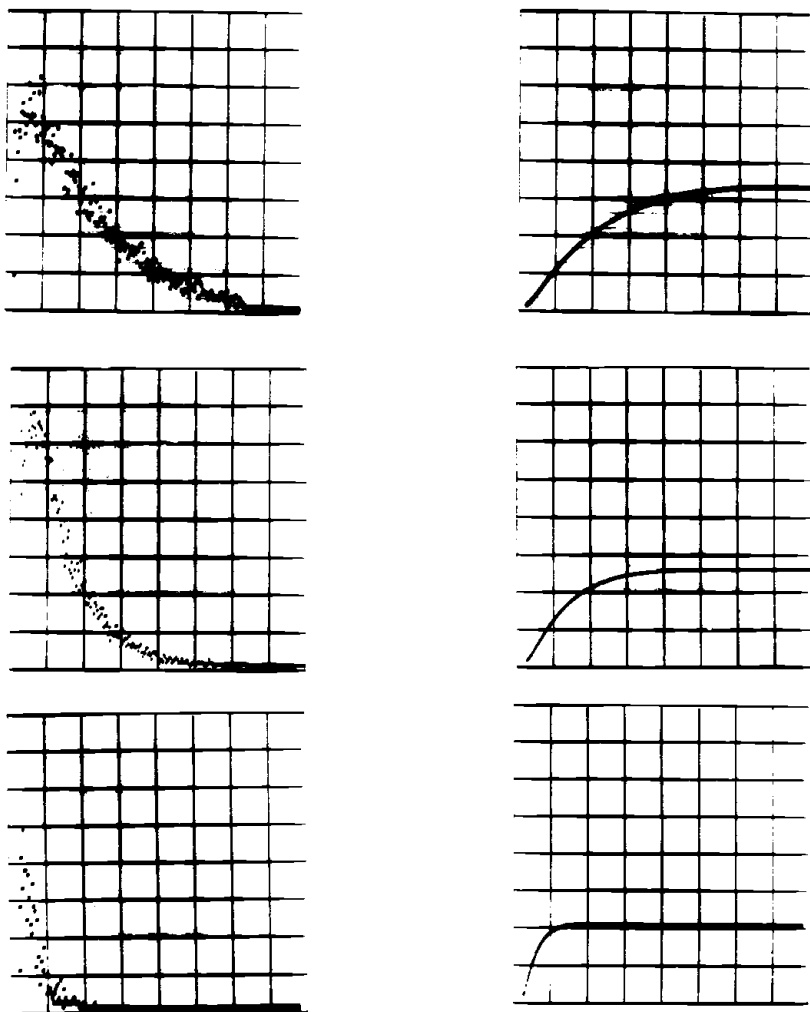


Figure 2. Spectra of  $^3\text{H}$ : effect of N-5 solubilizer (10% by volume).

Raw data are shown on the left and integrals of the spectra are on the right. In descending order samples are

- toluene - PPO, 7g/L ( $^3\text{H}$ -Toluene) equilibrated with  $\text{N}_2$ .
- toluene - PPO-7g/L - 10% N5
- toluene - 10% N5

Full scale for the two samples containing PPO was 256 counts/channel/2 min. For N 5 - toluene full scale was 64 counts/channel/2 min.

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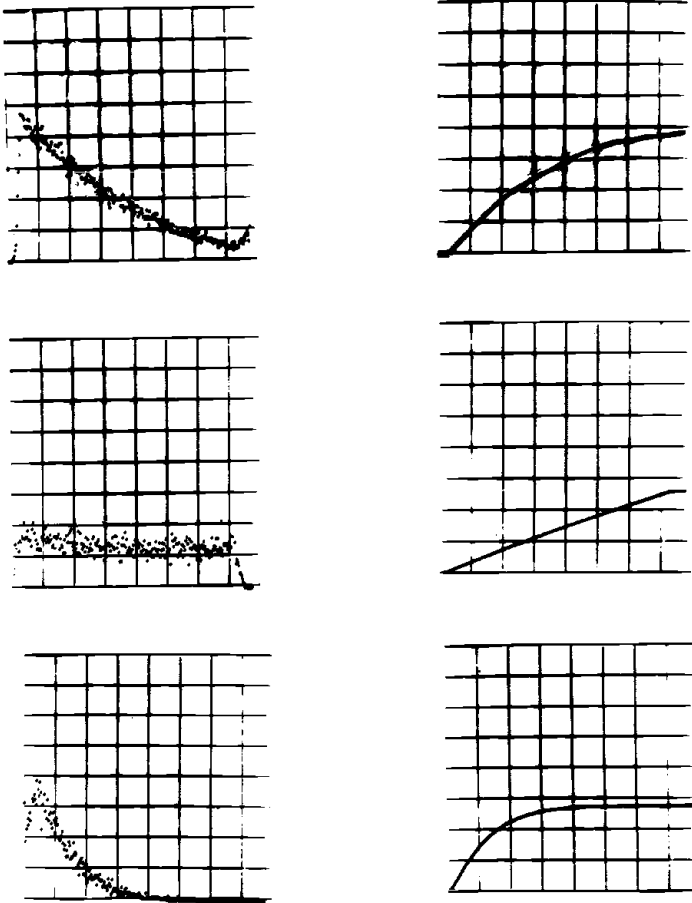


Figure 3. Spectra of  $^{14}\text{C}$ : effect of N-5 solubilizer (10% by volume).  
Raw data are on the left, integrals on the right  
- toluene - PPO, 7g/L ( $^{14}\text{C}$  toluene) equilibrated with  $\text{N}_2$   
- toluene - PPO-7g/L - 10% N5  
- toluene - 10% N5  
Full scale for the samples was 512 counts/channel/2 min.

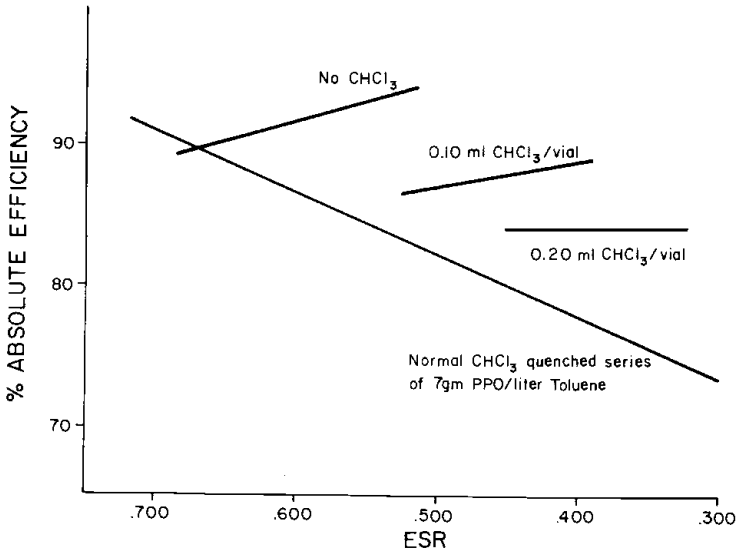


Figure 4. Effect of BBS-3 on a <sup>14</sup>C-toluene quench correction curve. The data are derived from Fig. 4, but are plotted without consideration for the concentration of BBS-3. Samples with increasing BBS-3 concentrations of course had lower ESRs inasmuch as BBS-3 itself contributed to impurity quenching. BBS-3 containing samples (indicated for each condition of impurity quenching by CHCl<sub>3</sub> fail to conform to the ESR standard curve (Ref.1)

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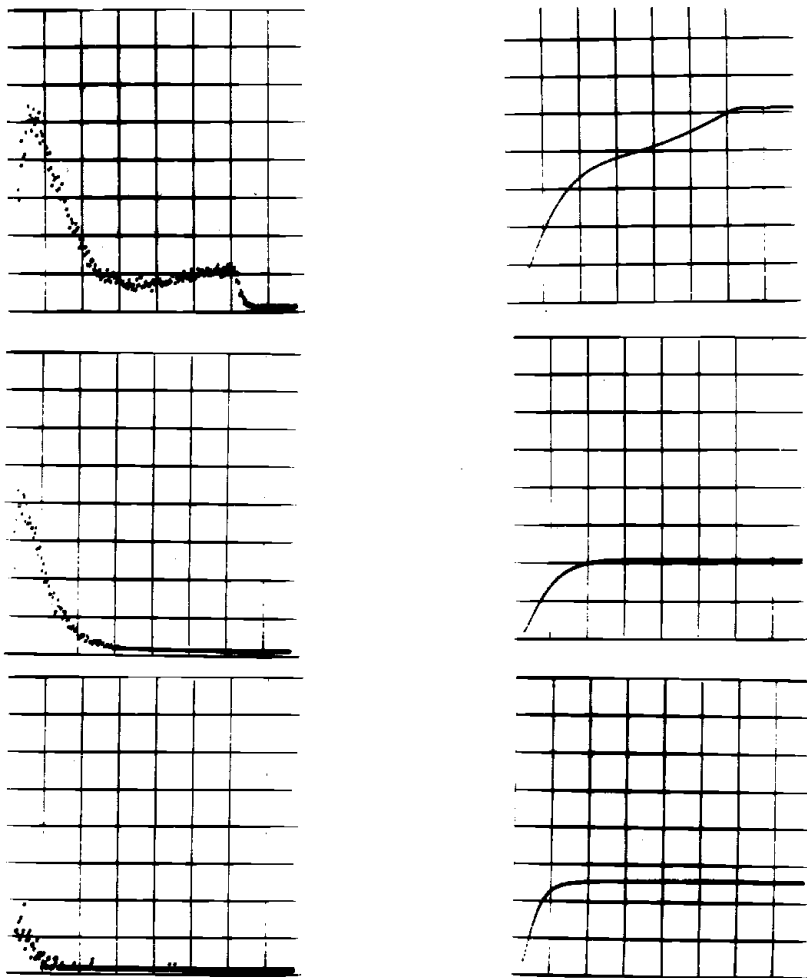


Figure 5. Spectra of  $^{125}\text{I}$ : effect of N-5 solubilizer (10% by volume).

- Raw data are shown on the left and integrals of the spectra on the right. In descending order the samples are:
- toluene - PPO, 7g/L - 10% N5  
(256 counts/channel/2 min. full scale) counting efficiency 66%
  - toluene - 10% N5 - (128 counts/channel/2 min. full scale) counting efficiency: 6%
  - toluene alone. (64 counts/channel/2 min. full scale) counting efficiency < 1% (See Figure 2).

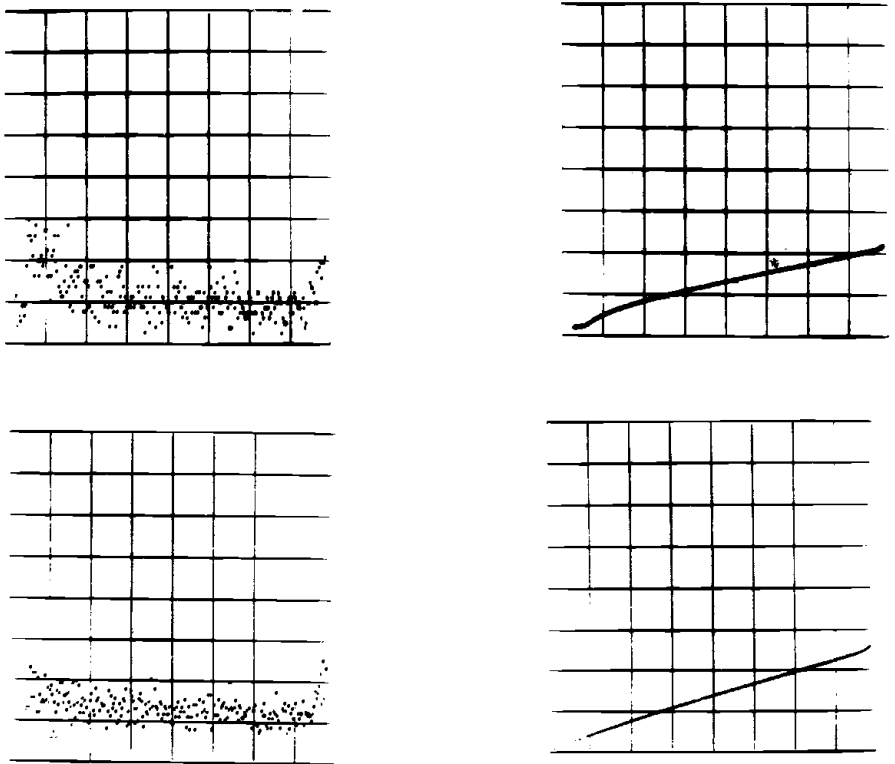


Figure 6. Spectra of  $^{131}\text{I}$ : effect of N-5 solubilizer (10% by volume).

Raw data are shown on the left and integrals of the spectra are on the right. The upper sample represents  $^{131}\text{I}$ -NaI in toluene - PPO 7g/L. and the lower toluene - PPO-7g/L-10% N5. Full scale in both cases is 512 counts/channel/2min. The lesser efficiency of the sample without solubilizer is attributable to incomplete solution of the sample.

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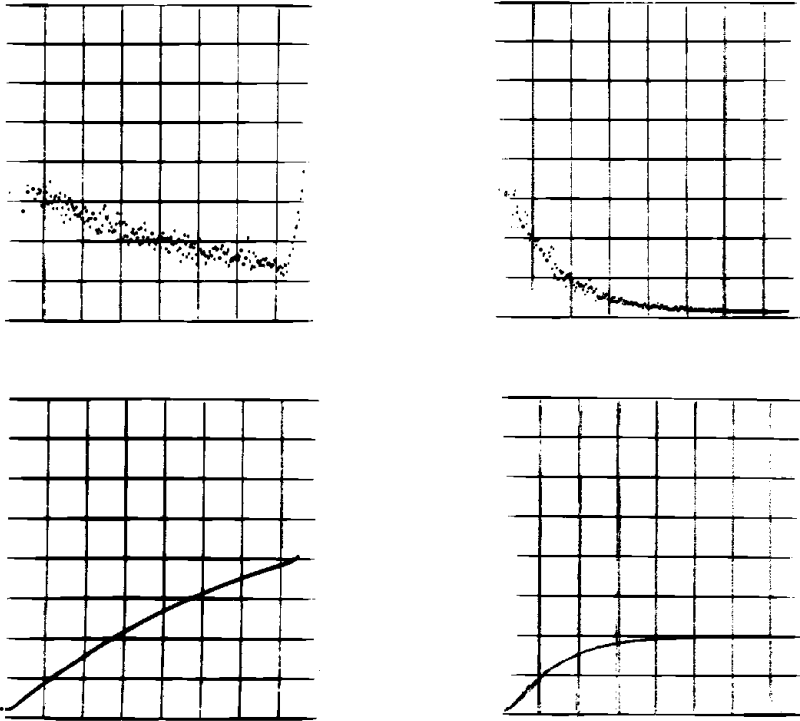


Figure 7. Spectra of  $^{131}\text{I}$  in toluene: effect of N-5 solubilizer.

Raw data are at the top, the integral plots below. The left represents a sample in toluene - 10% N5 counted at 96% efficiency (256 counts/channel/2 min. full scale). On the right, an incompletely dissolved sample of  $^{131}\text{I}$  in toluene alone.

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