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Final LDRD Report:

Scintillating Cocktail Mixtures and the Role of Water on the Optophysical Properties

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Final LDRD Report: Scintillating Cocktail Mixtures and the Role of Water on the Optophysical Properties

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Abstract

Two types of water-containing liquid scintillation mixtures were prepared in the present work. In the first, mixtures of 2-phenylethanol, water, diphenyl phosphate, sodium phenyl phosphate dibasic dihydrate, and the dye 2,5-diphenyloxazole (PPO) have been investigated as liquid scintillators. In the second system, nonionic and mixed surfactant systems were investigated in conjunction with water and small amounts of toluene. In both cases, increasing amounts of water led to reductions in the scintillation light yield.Understanding what factors contribute to this phenomenon is the focus of this report. Changes in the solution microphase structure, diminishing aromatic content of the cocktail mixtures, and inefficient energy transfer to the dye appear to be responsible for the decreased light yield as more water is added. In the 2-phenylethanol system, the observed experimental results are consistent with the formation of a bicontinuous microemulsion at higher water concentrations, which incorporates PPO and shields it from the quenching effects of the increasing polar matrix. Evidence for this proposed phase change comes from light

scattering data, photo- and x-ray luminescence measurements, and optical transparency measurements. In the surfactant-based system, the quenching effect of water was found to be less than both commercially-available dioxane-naphthalene mixtures used for scintillation counting as well as the 2-phenylethanol mixtures described above. The effect of different surfactant mixtures and concentrations were studied, revealing a beneficial effect upon the scintillation light yield for mixed surfactant mixtures. These results are interpreted in the context of reactive radical species formation following water ionization, which leads to light-yield quenching in aqueous systems. The presence of surfactant(s) in these mixtures enables the formation of organic-rich regions that are spatially separated from the reactive radicals. This hypothesis is consistent with subsequent experiments that showed reduced light-yield quenching in the presence of radical-trapping additives. A notable result from these surfactant studies was the preparation of an aqueous scintillator that was transparent and showed neutron/gamma pulse-shape discrimination. Section II below provides background information on the significance of this finding. The combined work described herein has implications on other efforts to make water-based solution scintillators—without aromatic content an efficient mechanism for ionizing radiation to sensitize emission from a dye is limited.

ACKNOWLEDGMENTS

We would like to thank two summer interns that helped with the collection of data— Nathaniel Curran Wilson and Trevor Kyle.

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NOMENCLATURE

[Sample list:]

PPO/DPO	2,5-Diphenyloxazole
SNL	Sandia National Laboratories
PL	photoluminescence
QY	quantum yield
DPP	diphenyl phosphate
Na2PP	sodium phenyl phosphate dibasic dihydrate
PhEtOH	2-phenylethanol
PMT	photomultiplier tube
nm	nanometer

Section 1. INTRODUCTION

Liquid scintillators are typically composed of aromatic organic compounds and one or more fluorescent molecules. These mixtures are based upon organic solvents that are often flammable or possess high vapor pressures. Additionally, the optical attenuation length of organic solvents are limited at or near the scintillator emission/peak photomultiplier tube response (PMT) wavelength. Applications that require large-scale scintillation detectors are particularly susceptible to these deleterious effects, resulting in reduced light collection efficiency and scintillation performance. For these reasons, liquid scintillation mixtures comprised of non-volatile, non-toxic and optically transparent ingredients are sought. This has been achieved to an extent with mineral oil-based scintillators, although the optical attenuation length of these materials is fundamentally limited by the transmission properties of the oil base (1 – 2 meters) Water is an idea candidate to address this limitation due to its very high transparency in the UV-vis region (optical attenuation length on the order of 20 meters in the scintillation emission range). The relative optical absorption properties for several liquids is provided in Figure 1, which obviates the choice of 2-phenylethanol and polyoxoethylene surfactants used in this work. However, energy transfer through aromatic moieties is required for efficient scintillation in organic-based scintillators, which has additional implications for other applications such as neutron/gamma particle discrimination. Furthermore, some mechanisms for particle discrimination rely on excited state triplet-triplet annihilation, which can be quenched by water. Heterogeneous liquid scintillation cocktails for tritium counting are not suitable for high energy gamma/neutron detection because of the short attenuation length and light scattering associated with micro-phase separation at higher water concentrations.

In this publication we report homogeneous scintillation cocktails containing both aromatic and aqueous components. Our goal was to make mixture capable of ionizing particle detection with high optical transparency near 420 nm. Our objectives include a) formulating a cocktail with low vapor pressure, flammability, and toxicity b) using inexpensive commercially available ingredients such as phosphate emulsifiers, non-ionic surfactants and 2,5-diphenyloxazole (PPO or DPO) fluorophores and c) benchmark light yield response compared to EJ-301. The role of phosphate emulsifiers and surfactants was to facilitate miscibility between the organic and aqueous phases, whereas the role of organic fluorophores was to provide a high fluorescence quantum yield for scintillation emission.

Section 2. THE ROLE OF AROMATIC MOLECULES ON SCINTILLATION COCKTAILS

In this section, we describe mixtures containing 2-phenylethanol (PhEtOH), Diphenyl phosphate (DPP), sodium phenyl phosphate (Na2PP), water and the fluorescent dye PPO. This combination of materials remains optically transparent over a while range of compositions. Scintillation light yield, photoluminescence and x-ray luminescence measurements coupled with physical properties' measurements of these mixtures gives us a rational to explain observations and design new liquid scintillators.

2.1. Cocktail Formulation: 2-Phenylethanol Compositions

To obtain homogeneous mixtures containing aromatic and aqueous content, we investigated numerous surfactants, salts, organic molecules, alcohols and water. We found a unique cocktail mixture based on 2-phenylethanol (an aromatic alcohol with a rose-like smell frequently used in cosmetics) and water (Figure 2). This solvent was chosen for further study on the basis of multiple factors, including low cost, low toxicity, aromatic content, and polar protic characteristics associated with the alcohol functional group. Completely homogeneous mixtures were possible for different ratios of diphenyl phosphate (DPP) and disodium phenyl phosphate (Na_2PP) in water. Organic fluors such as PPO could readily be dissolved in these mixtures at concentrations typically employed in traditional organic liquid scintillators (1-2 wt. %). Compositions used in this study were made by first creating two stock solutions; 1) PhEtOH/DPP at a 2:1 mass ratio and 2) water/Na2PP also 2:1 mass ratio.

A series of cocktail solutions were then made in 10 or 25-mL volumetric flasks. Briefly, each flask was charged with a fixed mass of PPO (25 or 65 mg for the 10 and 25-mL cocktails). The 1-mL of the stock organic solution (PhEtOH/DPP) was then added to dissolve the fluorophore followed by a fixed amount of the aqueous solution. The turbid mixture was then filled to 10 or 25-mL with the organic solution. The actual molar amounts of each component could then be calculated based on the original density and mass added of each solution. The concentration of PPO for every cocktail was also fixed. Four individually prepared cocktail series were made ranging from 0 to approximately 80% water by volume. Additional samples where made replacing PhEtOH with methanol to understand the roll of the aromatic content. Using a 7:3 vol/vol methanol and water mixture, 12 samples containing a fixed PPO concentration and varying Na2PP and DPP were made. Two samples were made with only Na2PP or DPP.

2.2. Cocktail Formation: Surfactant Compositions

Nonionic surfactants and mixed surfactant systems were prepared with water, toluene, and 2,5-diphenyloxazole (PPO) to form the scintillation mixtures studied in this section. Polyoxoethylene-based surfactants were selected due to their high optical transparency, low cost, low toxicity, and high carrying capacity for water. The molecular structures of Triton X-100 and SDS are shown in Figure 3. Other non-aromatic surfactants were explored but Triton X-100 gave the best results and is discussed here.

Two series of Triton X-100/Toluene/water were prepared. Series 1 contained a fixed 3:1 Triton/toluene ratio by weight with water added up to 18.5 weight percent (wt%). Series 2 contained a 9:1 Triton/toluene ratio with water added up to 51 wt%. The phase diagram in Figure 4 shows lines crossing both the microemulsion and liquid crystalline region where phase-stable optically transparent mixtures were achieved.[1] The dye PPO at 1 wt% was included in all mixtures.

Alternative compositions were prepared from these baseline mixtures by systematically varying the nature of the surfactant used, the identity of the organic fluorophore, and the presence of radical trapping additives. A mixed surfactant system comprising Triton X-100 and sodium dodecylsulfate (SDS, 6 wt. %) was also studied due to synergistic phase-stabilizing effects previously reported for this nonionic/ionic surfactant mixture.

2.3. Characterization of Cocktails: 2-Phenylethanol Compositions

The relative light yield for 13 samples (repeated three times) compared to EJ-200 was measured using a ^{137}Cs source and a Hamamatsu R1949-51 photomultiplier tube (PMT) operated at a voltage of -1900V. In addition, the following properties were measured: viscosity (cP); refractive index (N_D); optical transmission (by UV-Vis spectroscopy); excitation and emission spectra and emission quantum yields by photoluminescence spectroscopy; x-ray luminescence; and quasi-elastic light scattering.

2.3.1 Optophysical Properties

The relative scintillation light yield (LY) for PhEtOH/water samples as a function of volume of water is shown in Figure 5. Series A and B contained only eight samples. Series C – E contained 13 mixtures with more samples between 30 – 70 vol% water. The overall trend shows that with more water, the light yield decreases. This behavior is not unprecedented, as reduced light yields are typically encountered as a result of increased water content in liquid scintillation cocktails. Liquid scintillation cocktails are available commercially under trade names such as Ultima Gold. However, these materials are generally unsuitable for neutron and/or gamma-ray detection applications due to light-scattering constraints on the sample volume. In the present samples, the LY was found to unexpectedly recover between 40 – 60 vol% water, followed by a subsequent decrease at higher water concentrations. To understand this phenomenon, we measured the photoluminescence quantum yield and x-ray luminescence for each sample in series C – E.

The optical transparency of all 13 samples is shown in Figure 7. A significant solvatochromatic shift is observed as more water is added. At 410 nm the samples possess roughly similar light transmission values. At shorter wavelengths the addition of water improves the transmission with an abrupt increase near sample 6 when measured at 365 nm. Also plotted are data for 380 nm, which show a similar increase in transmission as water is added, followed by a leveling off after sample 7.

Photoluminescence measurements (emission, excitation and quantum yield) of the 13 samples show a nonlinear solvatochromatic shift similar to the UV-Vis data. Upon the addition of water a gradual blue shift in the excitation spectrum is observed for samples 1-6. This result is consistent with the relative absorption coefficients of water and phenylethanol, where water possesses negligible absorption between 350-480nm. In contrast, samples 7 – 13 are coincident, showing an excitation peak maximum at 357 nm (Figure 7) and nearly superimposable UV-Vis absorption spectra. A similar trend is seen in the emission spectra where a decrease in intensity and quantum yield is observed for samples 1 – 6. The emission wavelengths are coincident until sample 7, at which point a 35 nm jump in emission wavelength is observed. The quantum yield for emission also increases with sample 7. Plotted in the lower section of Figure 7 are the quantum yield data and maximum excitation and emission wavelengths for each sample.

The x-ray luminescence data for the 13 samples are shown in Figure 8. These data provide the emission spectra generated from interaction with ionizing radiation interaction (X-ray, gamma-ray, neutron). Integration of these spectra thus provides an accurate means to determine the relative scintillation light yields for each material. These data show a gradual decrease in the integrated emission intensity for samples 1 – 6 which recovers similarly near sample 6 – 8. The wavelength of emission also shifts from a maximum near 435 to 385 nm. While not coincident with the PL data, the trend is similar.

Next, 15 samples were made to understand the relationship between the aromatic content of the cocktail mixtures and the scintillation light yield. A 7:3 methanol/water (v/v) mixture was used because it solubilizes PPO at approximately 1 wt% and solubilizes high concentrations of either DPP or Na2PP. All data, including the normalized scintillation LY and photoluminescence quantum yield are plotted in Figure 9. Sample 1 with only PPO shows low scintillation light yield but high QY for emission upon direct excitation of the PPO. As more Na2PP is added, the scintillation LY increases but the QY remains nearly unchanged. Upon addition of DPP in sample 6 the LY and QY stay relatively high but in sample 7, with no Na2PP, both the LY and QY drop dramatically. Mixtures with no PPO (11 and 12) have a low LY similar to anything with DPP. Sample 13 with PPO and saturated with Na2PP shows the highest QY and LY. Again, upon addition of DPP the LY drops suggesting that DPP quenches emission from PPO. Tracking the scintillation LY with aromatic content shows some correlation as long as DPP is absent. The highest scintillation LY is seen from sample 13, which also shows a QY efficiency similar to samples 1 – 5.

Figure 10 shows the UV-Vis spectra of six samples in 7:3 MeOH/water, composed of Na2PP, DPP and PPO, similar to the compositions used for the 13 PhEtOH/water cocktail solutions. From these spectra it is clear that only PPO absorbs past about 285 nm. The extinction coefficient for PPO is approximately 1.5 orders of magnitude greater than either Na2PP or DPP and dominates the absorption. It is peculiar that the excitation maximum (λ_{ex} = 365 nm) for cocktail samples 1 – 6 (Figure 3) is at a longer wavelength than the peak absorption of PPO (λ = 305 nm) in methanol/water mixture. For reference, Berlman reported λ_{max} = 306 nm in cyclohexane. Only upon addition of more water to the PhEtOH/water cocktails does the excitation maximum shift to short wavelengths. More work is needed to understand these observations but it appears the water quenches the higher energy excitation band of PPO.

As more water is added the LY decreases because of two factors- decreasing aromatic content results in inefficient energy transfer upon ionization and two, water quenches the excited luminescent state of PPO. However, around samples 6 – 8 there is a phase change in the system from a homogeneous soluble state to a bicontinuous microemulsion. This is evident from the gradual changes in UV-Vis transmission and photoluminescences data which then undergo a more abrupt halt at sample 7. In sample 7 a proposed phase change occurs resulting in an increase in the light yield, possibly due to an increase in the transmission of the sample. This phase transition could also exclude water from the inner sphere of PPO, temporarily reducing water-based quenching.

The viscosity-corrected light scattering data show that no significant phase separation or particles are present in solution until sample 6, at which point an undetermined phase appears with a radius of hydration close to 3 nm Figure 11. This size could be the domain of a bicontinuous microemulsion with the majority phase being water/Na2PP and PhEtOH/DPP constituting the minor phase and also solubilizing PPO. When more water is added to the system a decrease in the LY is again measured but this is not due to quenching of the PPO excited state but rather due to a decrease in the aromatic content of the entire system. The photoluminescence and x-ray luminescence emission data and quantum yield data for samples 7 – 13 show that the addition of water does not affect these energy transfer processes. Only the bulk ionization of the cocktail mixtures measured via scintillation light yield are affected by the addition of water but this is attributed to decrease aromatic content.

2.4. Characterization of Cocktails: Surfactant Compositions

The light yields for the prepared scintillators were obtained using a ^{137}Cs source and a Hamamatsu R1949-51 photomultiplier tube (PMT) operated at a voltage of -1900V. Relative light yield values were calculated with reference to EJ-200 plastic scintillator, which possesses a light yield of 10,000 photons/MeV electron equivalent. The Compton edge positions for the respective scintillators were compared for the liquid samples in quartz cuvettes that were coupled to the PMT face using Visilox V-788 optical grease. UV-Vis absorption/transmission data were collected using a Shimadzu UV-3600 Plus spectrophotometer. Steady-state and fluorescence timing measurements were obtained using a Horiba Jobin-Yvon FL3-21 fluorimeter. These measurements were collected at 90^{o} to the incident excitation, whereas fluorescence quantum yield data were obtained using an integrating sphere.

Series 1 with a fixed 3:1 ratio of Trion X-100/toluene formed stable microemulsions up to 18.5 wt% water. The normalized relative light yields for seven samples are plotted in Figure 12. Also plotted are the normalized aromatic content of the mixtures and wt% water. The slopes for these data show that the light yield drops faster than the aromatic content implying that the decrease in light yield is not simply a dilution effect. Water or radiolysis products likely reduce the light yield by some energy transfer mechanism.

Series 2 scintillation pulse-height spectra are shown in Figure 13 for two scintillator compositions based on Triton X-100/Toluene/PPO. The black trace in this plot corresponds to a scintillator composed of 89% w/w Triton X-100, 10% w/w Toluene, and 1% w/w PPO. This baseline composition contains no added water and has a relative light yield 73% that of EJ-200 (not shown). The reduced light yield vs. EJ-200 indicates that there is a modest extent of quenching associated with Triton X-100 in place of toluene or polystyrene in liquids or plastic scintillators, respectively. This result is consistent with the 2-phenylethanol scintillator findings described above, where decreasing aromatic content is associated with decreased scintillation yields. In this case, the reduced aromatic content is due to the polyoxoethylene portion of the Triton X-100 surfactant. The red trace in Figure 13 represents a similar Triton X-100 composition as the baseline mixture, with the exception of 16.7% w/w water added to replace a corresponding amount of Triton X-100. The light yield was found to decrease by 15%, as shown by the shift in the Compton edge position (dotted lines in Figure 13). Further experiments were thus performed with the goal of determining whether this reduction was due to (1) 'chemical' quenching by H_2O and its radiolysis products, (2) decreased aromatic content associated with dilution by water, or (3) a combination the these considerations.[1]

The light-yield data as a function of water content is shown in Figure 14 for surfactant-based scintillators containing 0-51 wt. % water. Similar data are shown in this plot for a dioxane-naphthalene reference scintillator and a 2-phenylethanol based scintillator composed of Ph-EtOH, H_2O, DPP (13.5 wt. %), Na_2PP (13.5 wt. %), Toluene (4 wt. %), and PPO (0.7 wt. %). Dioxane-naphthalene comprises a scintillation composition previously reported in liquid scintillation counting due to its ability to solubilize up to 25 wt. % water without phase separation. The light-yield data indicate the dioxane-naphthalene has the highest starting light yield at 0% water (81% EJ-200), although it exhibits the steepest decline upon water addition. This effect is consistent with a 'chemical quenching' mechanism by water and its radiolysis products (i.e. hydroxyl and hydrogen radicals). Interestingly, the slopes of the surfactant-based and phenylethanol-based scintillators are similar to each other and significantly smaller than dioxane-naphthalene. The calculated rate of light yield decrease in these materials is modestly greater than one would expect based upon simple dilution alone, which indicates the possibility of both dilution and chemical quenching mechanisms. For example, the surfactant-based mixture at 51 wt. % water exhibits a light yield 44% that of the baseline 0% water composition. Although the origin of this behavior is not yet fully understood, this finding represents a significant advance to existing liquid scintillator materials due to the combination of higher light yield and higher water carrying capacity before phase separation. The latter point is of key importance for large-scale scintillators due to requirements of large optical path length and minimal light scattering.

Prior work has shown that mixed surfactant mixtures possess enhanced thermodynamic stability relative to analogous compositions based on either pure surfactant alone.[2] One measure of this is the critical micelle concentration (CMC), which represents the minimum surfactant mixture required for spontaneous self-assembly of micelles in a water medium. These values are shown in Table 1 for a series of nonionic and ionic surfactants and mixtures thereof. The highlighted entries indicate CMCs that are more than two orders of magnitude smaller (more stable micelles) than either pure surfactant alone. This enhancement in micelle stability has been associated with cooperative interactions between nonionic and ionic surfactants at the phase boundary. [2] While the concentrations used in this work are significantly greater than the CMC, these cooperative interactions between surfactants will result in a stronger diffusion barrier between aqueous and organic regions.

Another series of experiments were thus conducted to assess the effect of mixed surfactants upon the scintillation properties. Representative results are shown in Figure 15, which provides the pulse-height spectra for 0-51 wt. % water compositions. The black and blue traces correspond to 0% water and 37% water with Triton X-100 as the sole surfactant. The red and green traces correspond to 37% water and 51% water in the presence of Triton X-100 and sodium dodecylsulfate (SDS) as the mixed surfactant mixture. The results show that there is a significant enhancement in the observed light yield following co-surfactant addition. At 37 wt. % water, the addition of 6 wt. % SDS led to a light yield that was more than two times greater than the analogous Triton X-100-only composition. The addition of more water up to the 51 wt. % phase-separation limit showed only minimal decreases in the light yield relative to the 37% water data.

Several organic fluorophores were considered in efforts to maximize the light yield and to understand the relevant structure-property relationships of the fluorophore structure. Table 1 summarizes several relevant parameters, which include the Förster radius (R_0), fluorescence quantum yield, radiative lifetime, and relative scintillation light yield. The Förster radius is a measure of the distance at which fluorescence resonant energy transfer is expected to be efficient between the host matrix and the fluorophore. This value takes into account several parameters which include the donor quantum yield, donor lifetime, acceptor absorption coefficient, and fluorescence quantum yields. Consequently, the larger a Förster radius indicates more efficient energy transfer and therefore more efficient scintillation. This parameter is sufficient to explain the qualitative trends for all fluorophores except for the observed light yields obtained for PBD versus PPO. In this case, another factor must be responsible for the higher light yield of PPO. It is possible that the oxidation potential is a relevant parameter to explain this result, as water is known to produce reactive radical fragments following interaction with ionizing radiation. These radicals may then react with the organic fluorophores to produce non-luminescent or even actively quenching compounds.

To further investigate this possibility, two types of radical scavengers were employed in the scintillation mixtures. The first radical scavenger was *tert*-butanol, which forms a stable radical following interaction with hydroxide radical. This radical scavenger has previously been used in pulse radiolysis of oxygenated aqueous systems.[3] The second was Vitamin C, an antioxidant with a much lower oxidation potential than any of the organic components in the scintillator. Possible reactions between Vitamin C and hydroxyl radicals are shown in Figure 17. Note, the actual mechanism for radical scavenging by Vitamin C is pH dependent. Higher scintillation light yields were observed for water-based scintillation mixtures that contained between 2-3 wt. % *tert*-butanol or Vitamin C, as shown in Figure 18 and Figure 19.

While a high light yield is the primary design criterion for a scintillator development effort, neutron/gamma particle discrimination is a critical secondary application for organic-based materials. Particle discrimination in organic materials is dependent upon two different mechanisms for light generation, the first corresponding to fluorescence emission following de-excitation from the excited singlet state. The second mechanism is associated with the fusion of two triplet excitons formed by the recombination of ionized states. This is an intrinsically low probability mechanism due to the requirement of high triplet density and mobility through the material. For example, the presence of defects in molecular crystals or oxygen in liquid scintillator systems is known to strongly quench the excited triplet states due to trapping and paramagnetic interactions. For this reason, it was of interest to probe the effect of water addition upon the particle discrimination properties of liquid scintillation mixtures. To our knowledge, neutron/gamma particle discrimination has not been reported in any water-containing scintillators to date. We hypothesized that particle discrimination may have been prevented in prior water-containing materials due to efficient triplet trapping by paramagnetic radical species following water ionization. The incorporation of surfactants to spatially separate the water-rich and organic-rich domains was considered as a route towards suppressing these deactivation pathways. Relevant particle discrimination results are shown in Figure 20 for a Triton X-100/Water/Toluene (10 wt. %)/ PPO (1 wt. %) scintillation mixture containing 0-16.7 wt. % water. This figure is a scatter plot of neutron/gamma discrimination performed according to the charge-comparison method. The upper distribution of each plot corresponds to the fast neutron events, whereas the lower distributions correspond to gamma-ray events detected for an AmBe radiation source. Although a slight reduction in the neutron/gamma separation is observed upon the addition of water, these results are the first known demonstration of this property in a transparent water-containing scintillator. It is significant to note that this composition required 5 wt. % PPO, which is significantly greater than the 1-2 wt. % typically used in traditional liquid scintillator compositions. This result is consistent with the occurrence of residual triplet trapping, as higher PPO concentrations are expected to provide a higher probability for successful triplet-triplet annihilation via an increase in the number of triplet states capable of transport.[4] Unfortunately, the higher PPO concentration limited the maximum water concentration for this system to only 16.7 wt. %. These results suggest that improved PSD at higher water ratios will only be possible if one is able to increase the extent of dehydration in the organic-rich regions of the surfactant-based scintillator.

Section 3. FIGURES

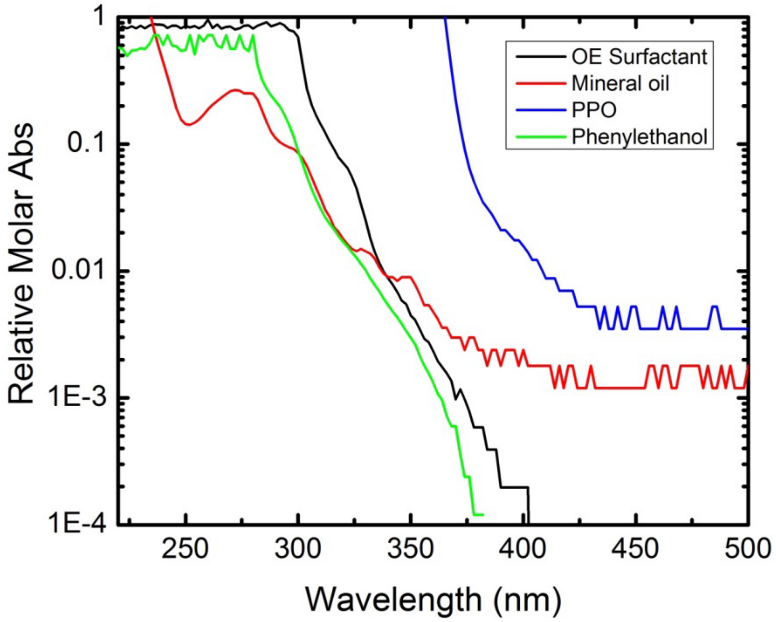


Figure 1: Relative UV-Vis absorption spectra for different liquid scintillator constituents.

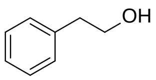
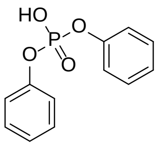
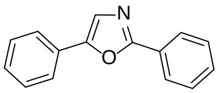
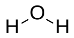
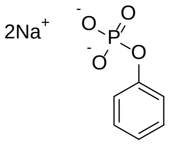
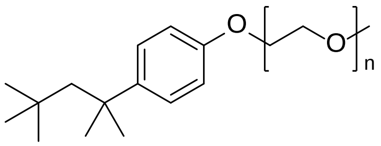
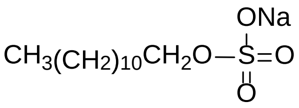
Primary Component	Solid additive	Fluoro (dye)
 2-phenylethanol "PhEtOH"	 diphenyl phosphate "DPP"	 2,5-diphenyloxazole "PPO" or "DPO"
 dihydrogen oxide "water"	 dibasic sodium phenylphosphate "Na2PP"	

Figure 2: Four component cocktail mixture ingredients plus dye



Triton X-100



$CH_3(CH_2)_{10}CH_2O-\overset{ONa}{\underset{O}{S}}=O$

sodium dodecylsulfate

Figure 3 : Molecular structures of surfacts employed in this work

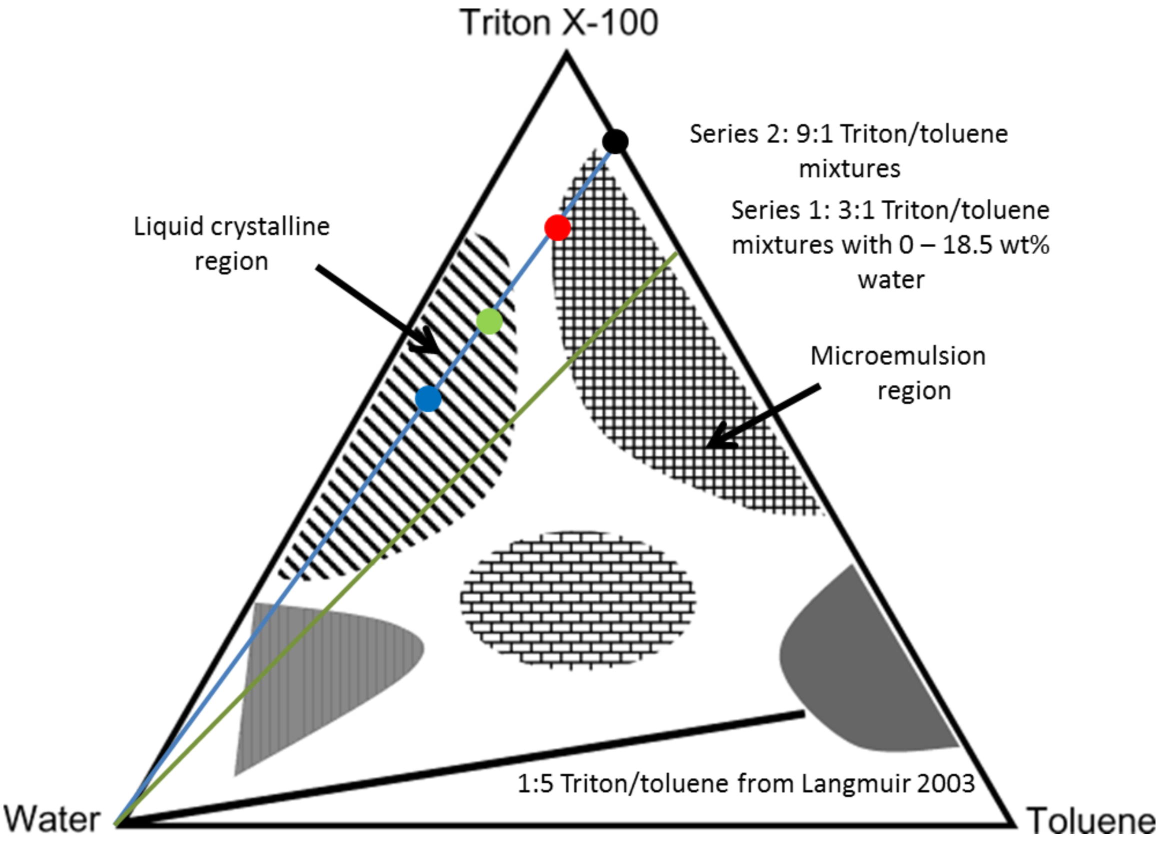


Figure 4: Ternary phase diagram for Water/Triton X-100/Toluene mixtures. The different shaded regions represent phase boundaries, whereas the colored circles correspond to the compositions studied in this work. Phase diagram adapted from (E-H. Liu, P.T. Callaghan, K.M. McGrath *Langmuir* 2003, 19, 7249-7258.)

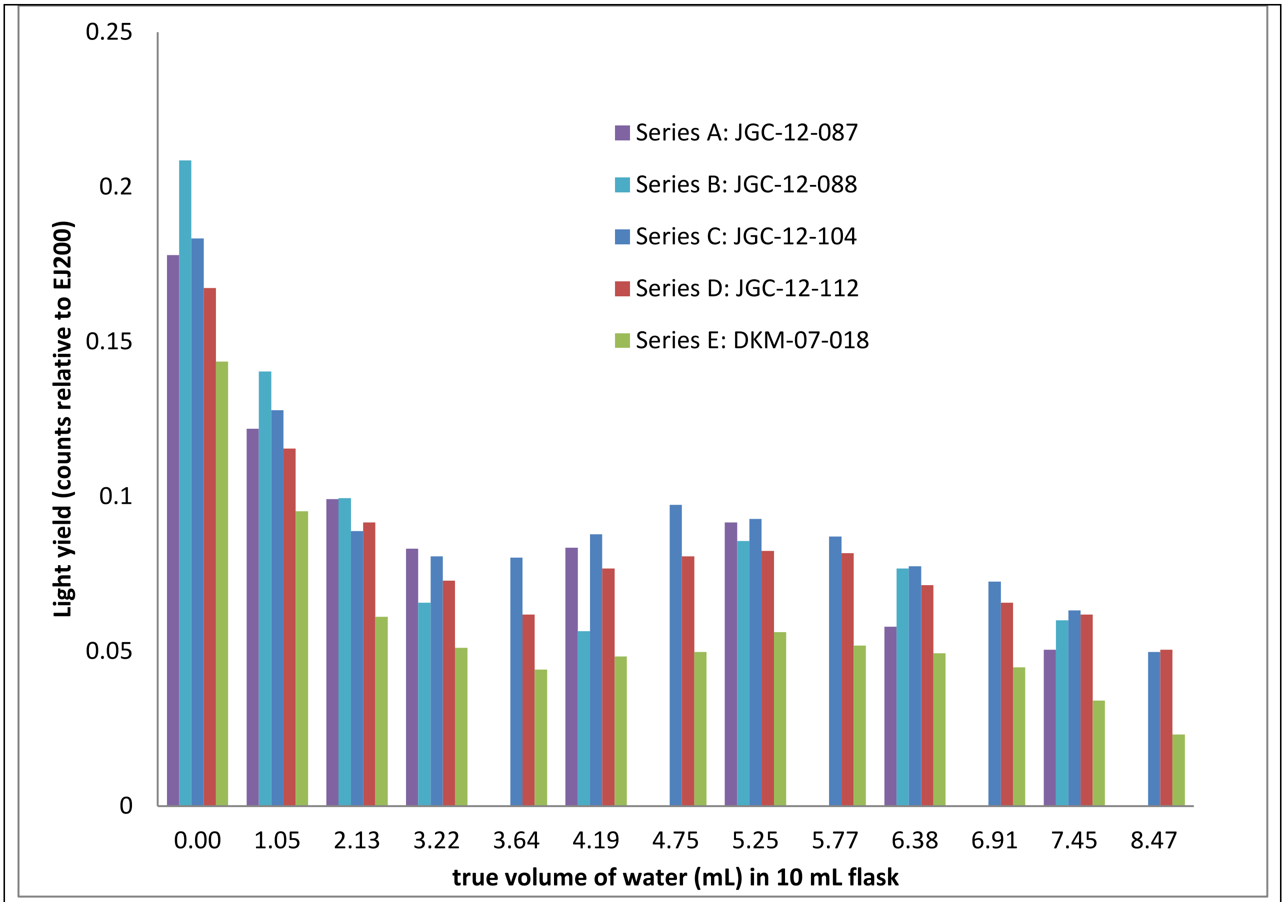
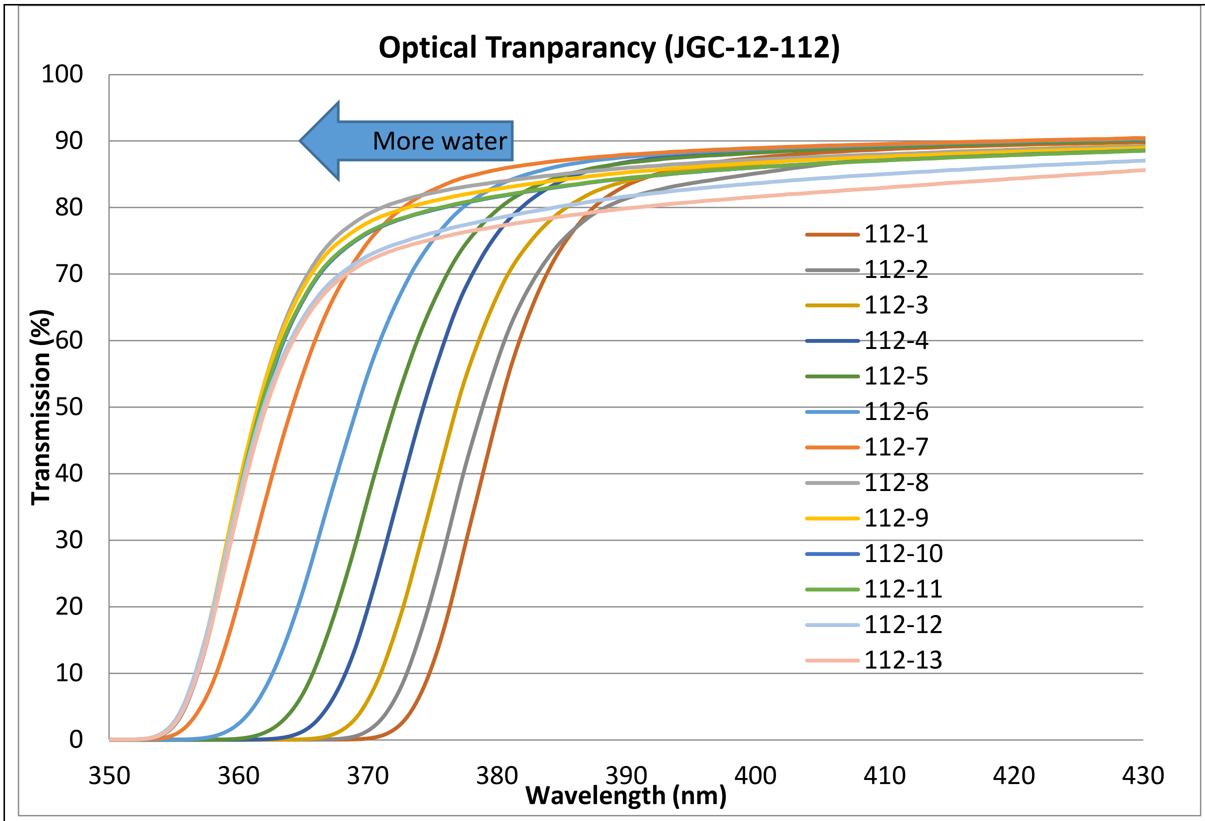


Figure 5. Relative scintillation light yield data for all samples



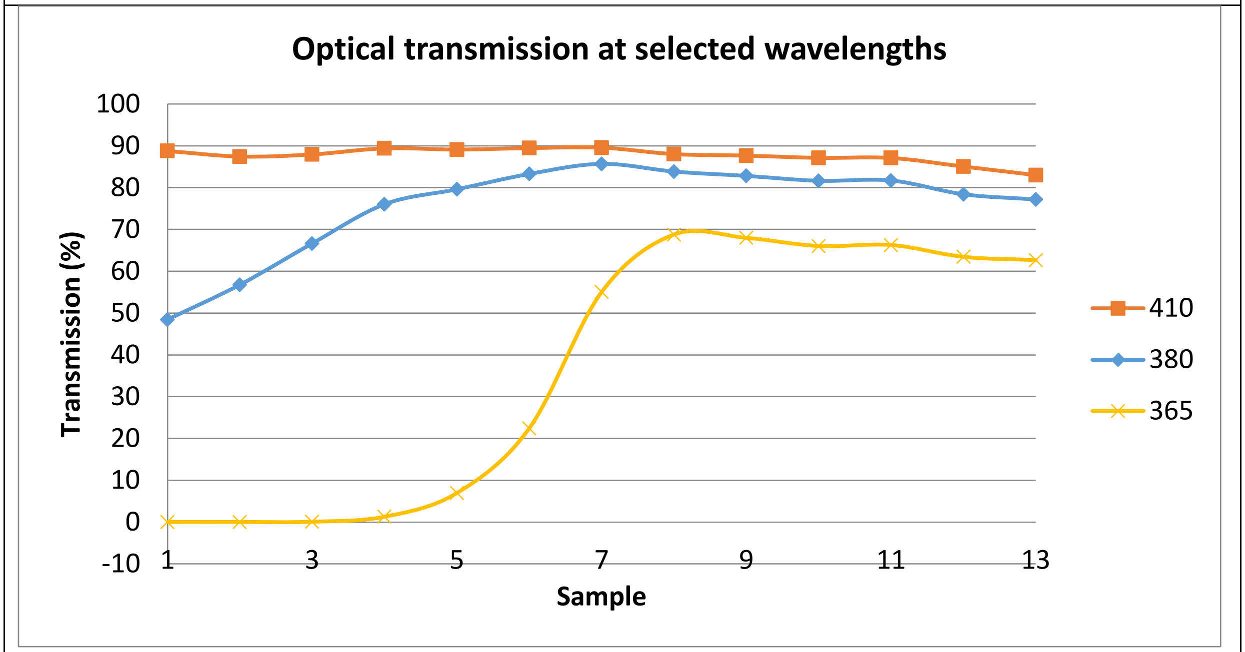


Figure 6. Optical transparency of cocktail mixtures as more water is added. Top shows entire spectrum. Bottom shows values at selected wavelengths

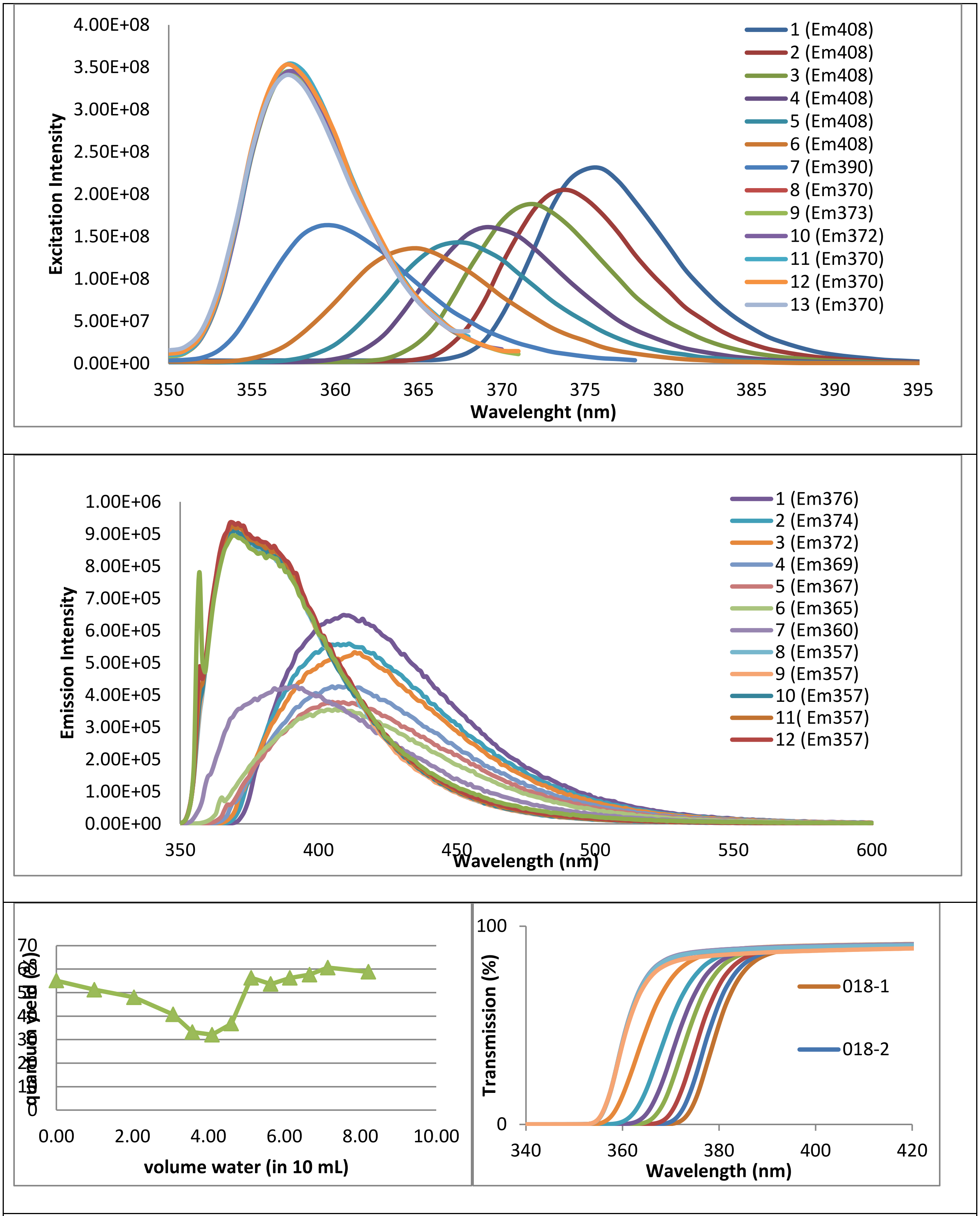


Figure 7. Excitation (top), emission (middle), quantum yield (bottom left) and optical transparency (bottom right) as a function of sample for series E.

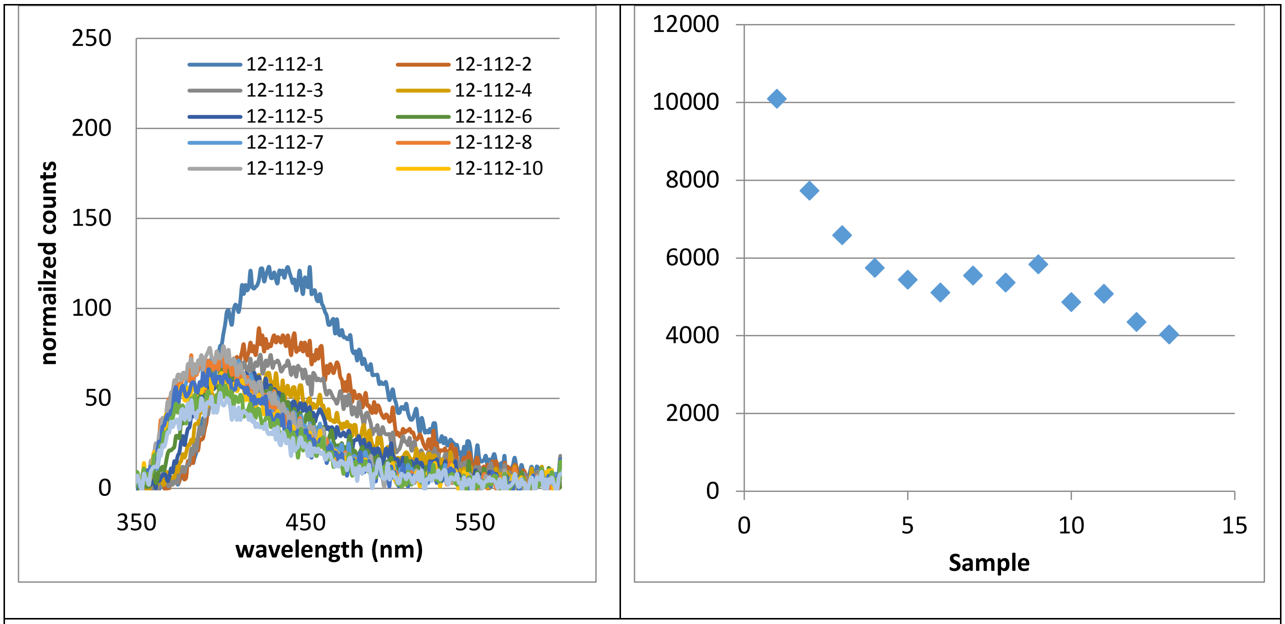


Figure 8. X-ray luminescence (left) and integrated data for 13 PhEtOH/water cocktail mixtures.

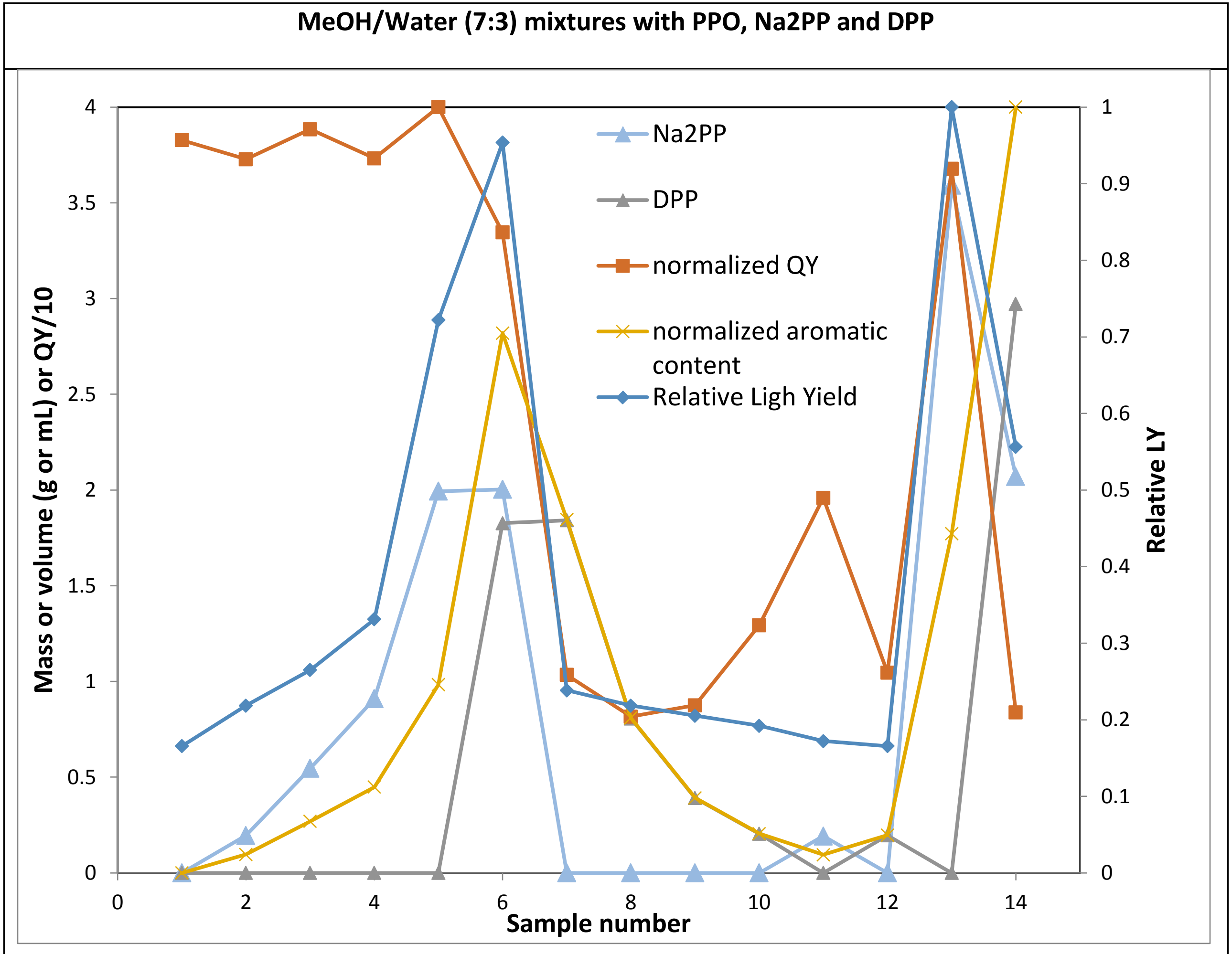


Figure 9. Various methanol/water samples with added Na2PP, DPP fixeed PPO plotted on major axis with measured scintillation or photoluminescence quantum light yield on minor axis. Samples 11 and 12 have no PPO.

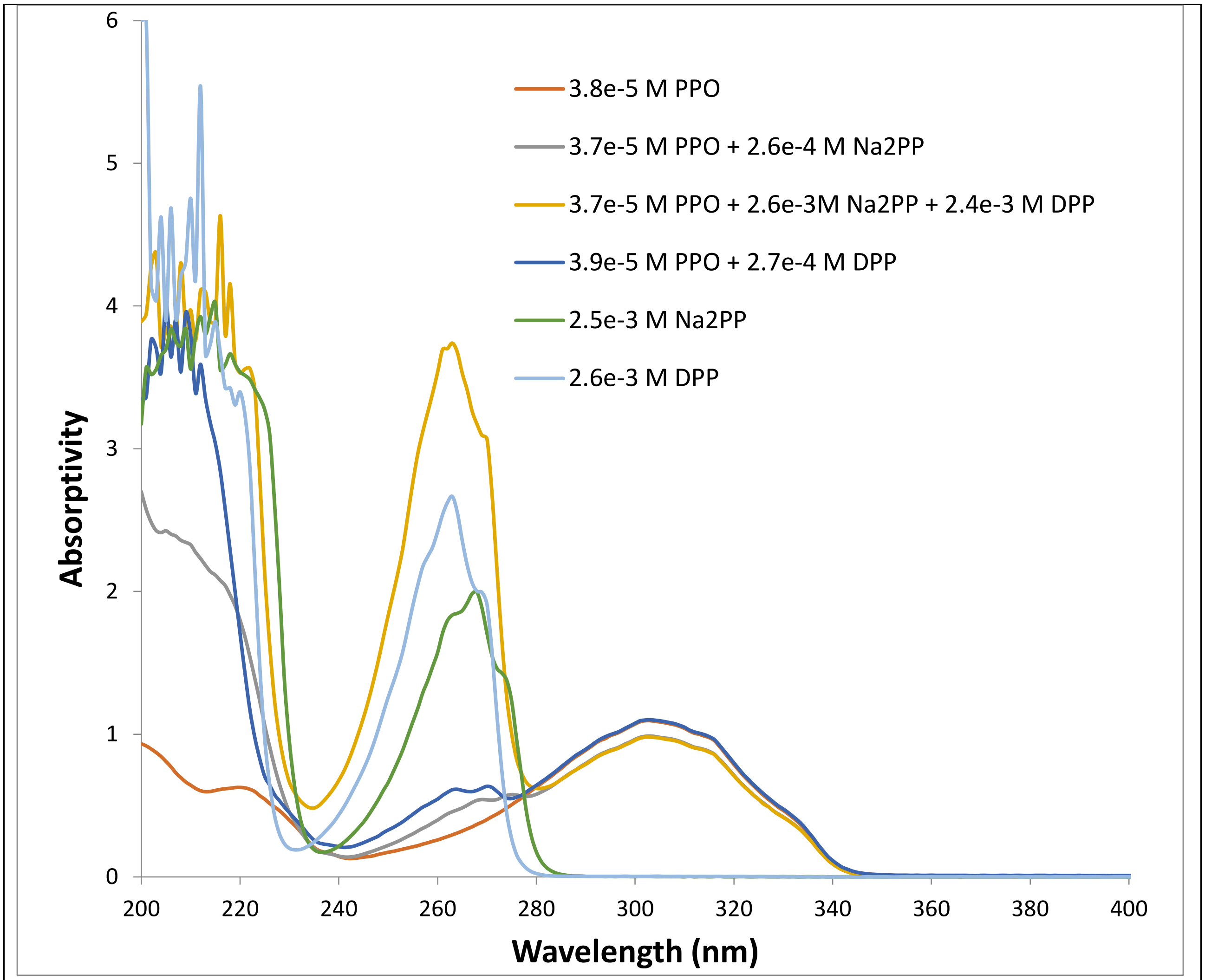


Figure 10. UV-vis spectroscopy data for six methanol/water samples

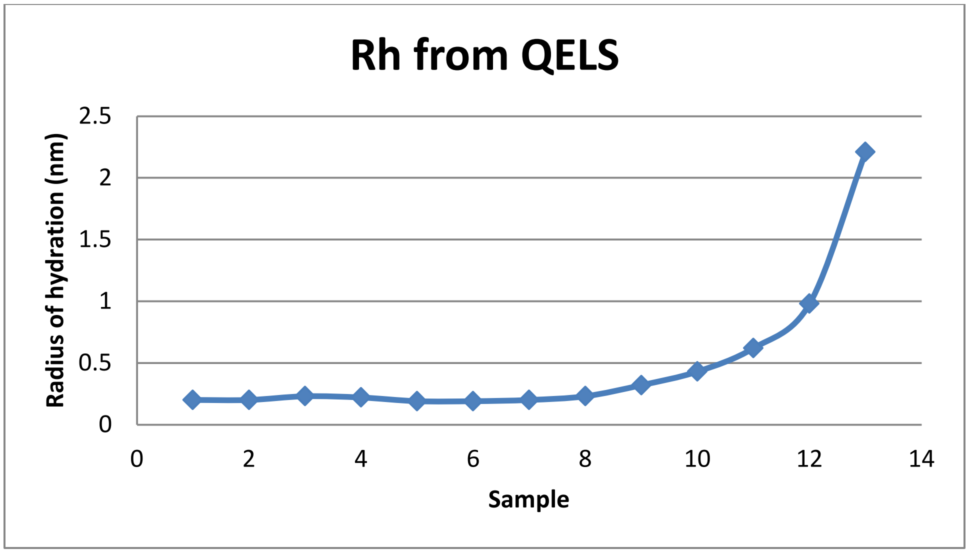


Figure 11: Radius of hydration of 13 PhEOH/water samples collected using a Wyatt QELS instrument. Data corrected for viscosity and refractive index changes

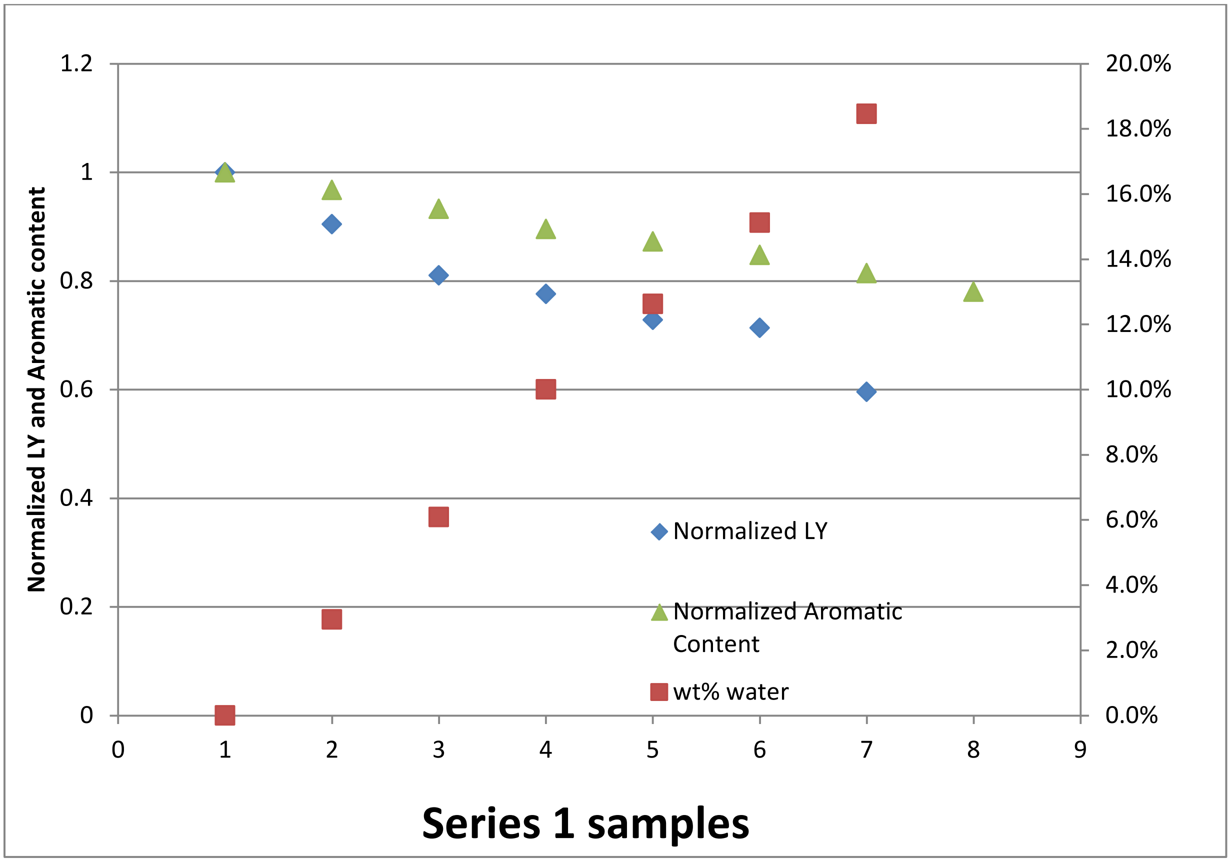


Figure 12: Plot of normalized light yield, aromatic content and wt% water in 3:1 wt% Triton X-100/toluene mixtures. Compositions fall in the stable microemulsion region.

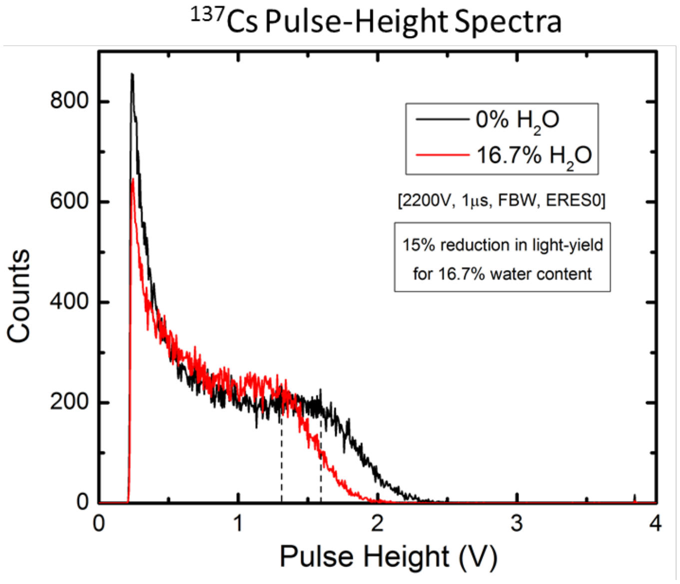


Figure 13. Scintillation pulse height spectra for a particle-discriminating liquid scintillator composition

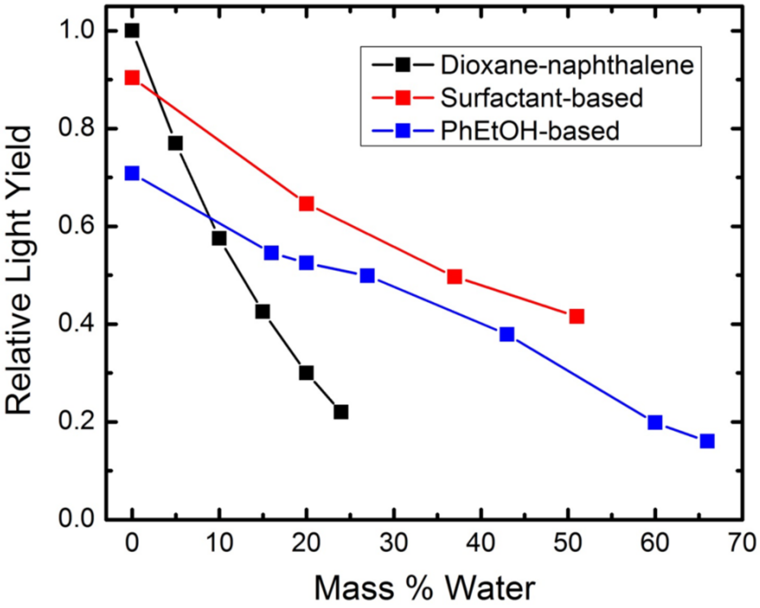


Figure 14. Relative light yield versus wt. % water calibration curves for three different aqueous scintillator systems. The endpoints for each curve correspond to the highest possible water content before phase separation. The dioxane-naphthalene system comprises reference scintillator used for aqueous scintillation counting samples.

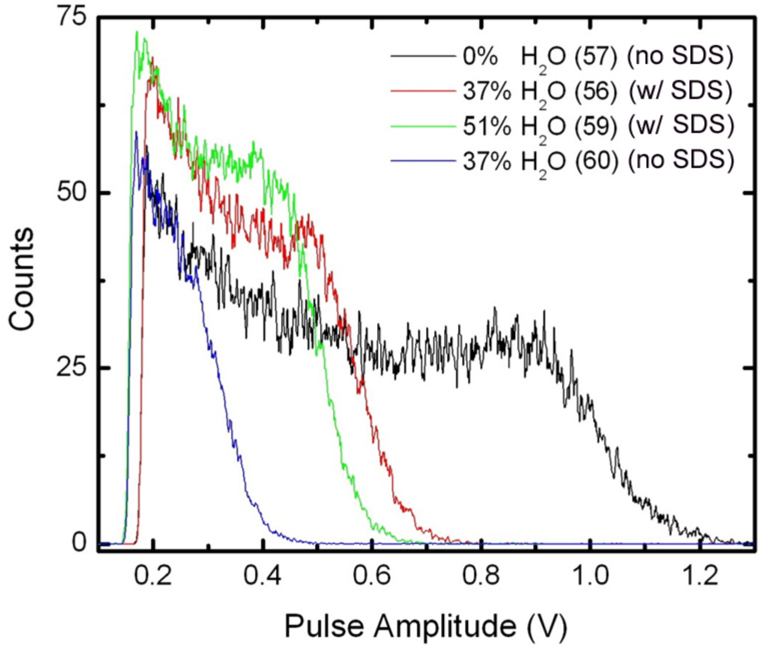
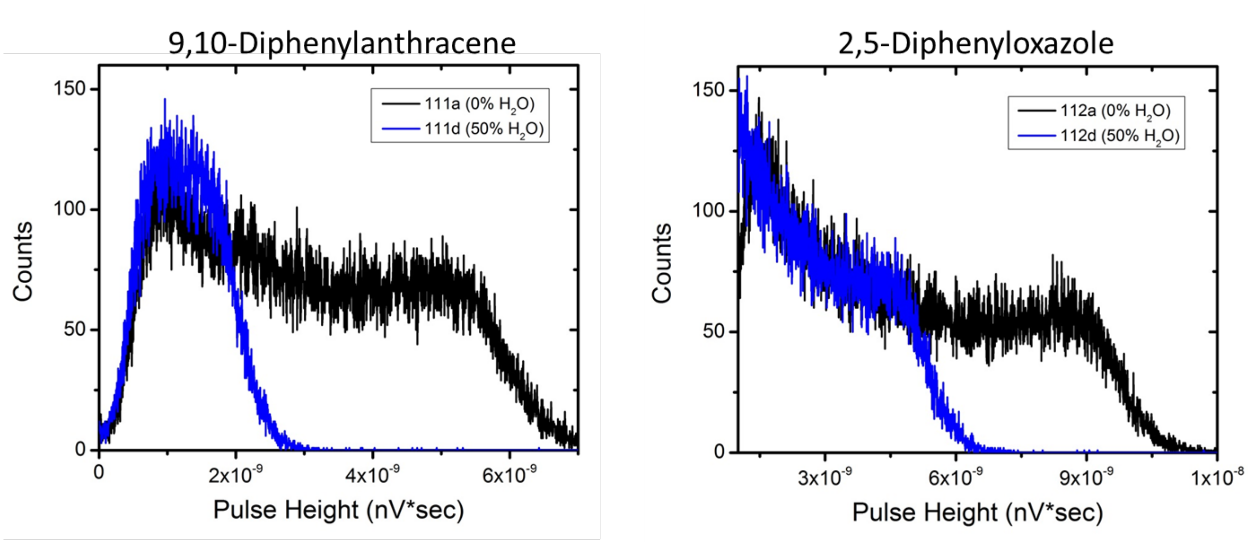


Figure 15 ^{137}Cs scintillation pulse height spectra for Triton X-100/Toluene/H_2O/PPO mixtures containing from 0-51 wt. % water and in two cases 6 wt. % SDS co-surfactant (red, green traces). Increased light yields are observed following water addition in the mixed surfactant system in comparison to Triton X-100 alone.


9,10-Diphenylanthracene

2,5-Diphenyloxazole

Figure 16. Comparison of the ^{137}Cs scintillation pulse height spectra for analogous aqueous scintillator compositions based on 9,10-diphenylanthracene and 2,5-diphenyloxazole fluorophores, respectively.

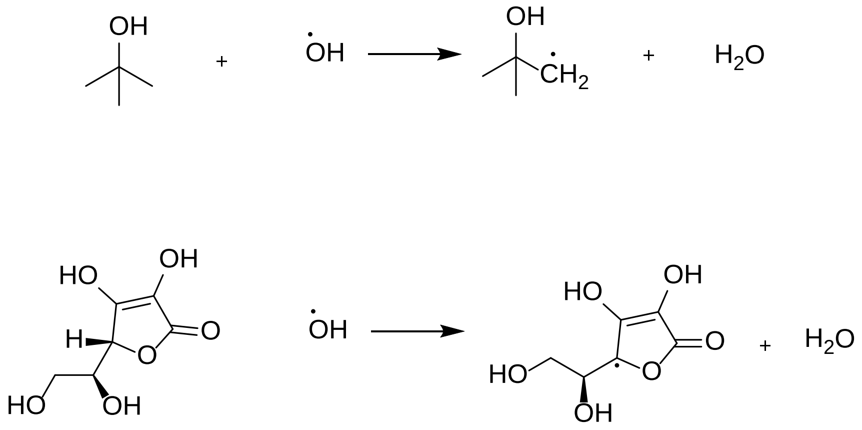


Figure 17. Free radical reaction between top) tert-butyl alcohol bottom) Vitamin C and hydroxyl radical

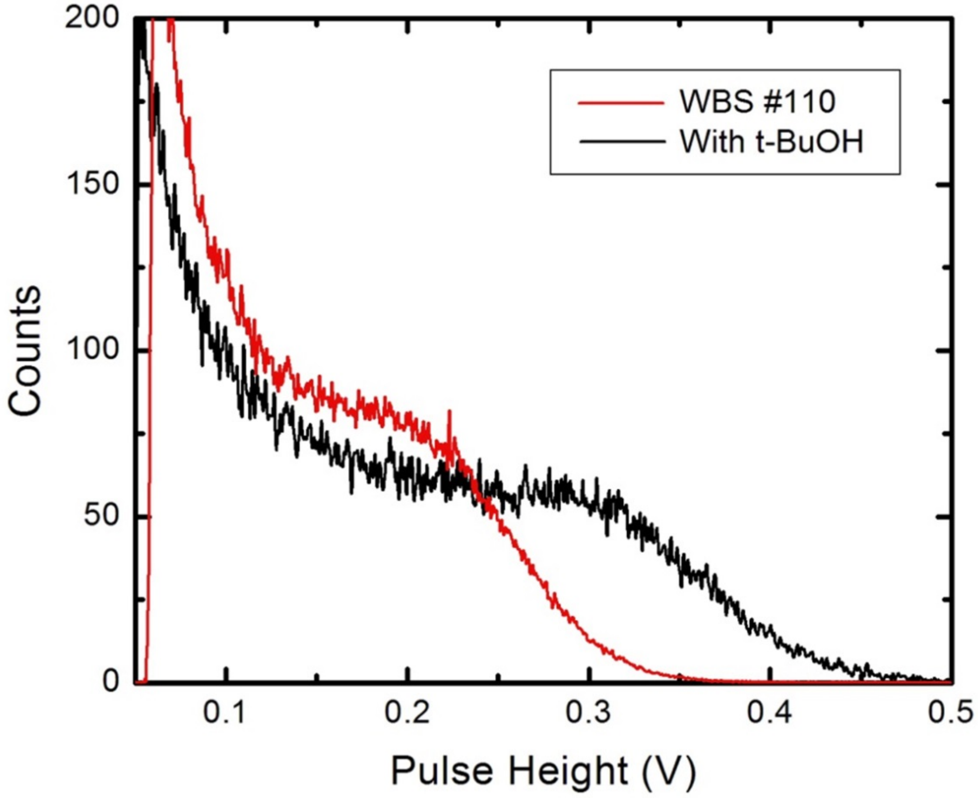


Figure 18 ^{137}Cs scintillation pulse height spectra for a 37 wt. % water-containing scintillator composition with and without 2 wt. % tert-butanol added as a radical scavenger.

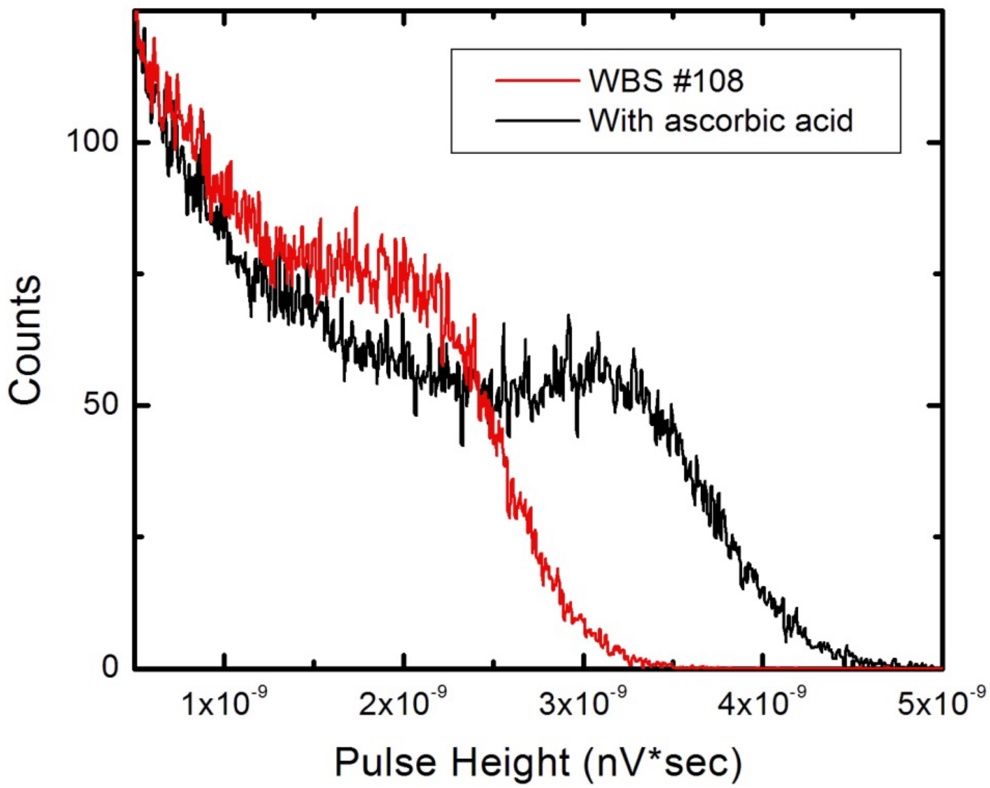
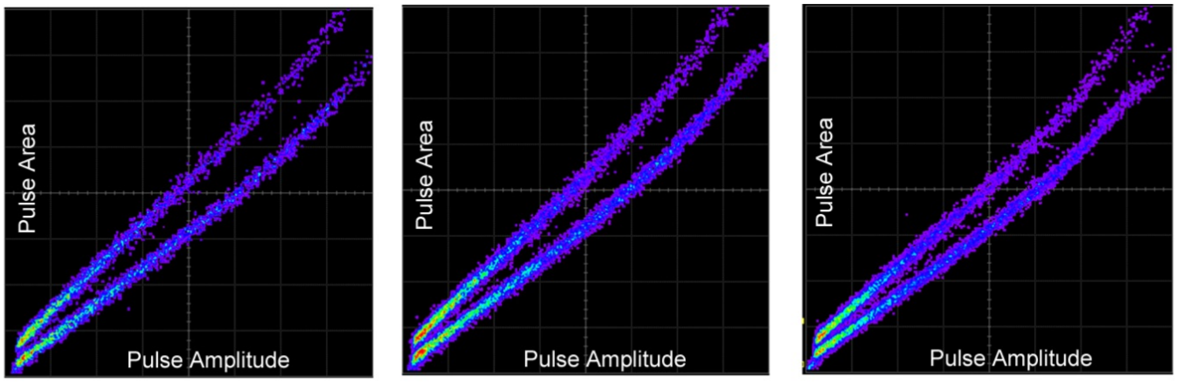


Figure 19 ^{137}Cs scintillation pulse height spectra for a 37 wt. % water-containing scintillator composition with and without 3 wt. % vitamin C added as an antioxidant.



- 0% H_2O
- 9.5% H_2O
- 16.7% H_2O

Figure 20 Neutron/gamma-ray pulse-shape discrimination histogram plot obtained for 0-16.7 wt. % H_2O liquid scintillation mixtures with an AmBe source. The upper and lower distributions in each figure correspond to fast neutron and gamma-ray events, respectively.

Table 1: Summary of properties for different organic compounds.

Acceptor Molecule	R_0 (Angstroms)	Q.Y.	Lifetime (ns)	Emission (nm)	E_{ox} (V)	Relative Scintillation L.Y.
Toluene (donor)	N/A	0.17	34	290	1.78	N/A
Anthracene	13.22	0.36	5.7	430	0.73	0.42
Naphthalene	18.54	0.23	65	334	1.14	0.58
9,10-diphenylanthracene	18.93	1.0	7.6	425	1.22	0.64
PBD	28.29	0.98	1.9	364	1.67	0.81
PPO	26.41	1.0	2.2	365	1.86	1.0

Table 2 Critical micelle concentrations for single component and mixed surfactant systems. Data taken from (C.C. Ruiz et al. *Mol. Phys*. 1999, 97, 1095)

Component 1	Component 2	cmc (mM)
4-Octylphenol ethoxylate (OE)	-----	0.18
Cetylpyridinium Chloride (CPC)	-----	0.98
Cetyltrimethyl-ammonium chloride (CTAC)	-----	1.24
Sodium dodecyl sulfate (SDS)	-----	8.14
Sodium dodecylbenzene sulfonate (SDBS)	-----	2.23
OE	CPC	0.0013
OE	CTAC	0.0016
OE	SDS	0.0021

Section 4. REFERENCES

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4. Horrocks, D.L., Pulse Shape Discrimination with Organic Liquid Scintillator Solutions. *Applied Spectroscopy* **1970**, 397-404.

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