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Phase stability and lithium loading capacity in a liquid scintillation cocktail

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Abstract

Liquid scintillation cocktails loaded with neutron capture agents such as ^6Li are used in both neutron and neutrino detectors. For detectors designed to operate over extended timespans, long-term stability can be a concern. We demonstrate the identification of thermodynamically unstable emulsions as distinct from stable microemulsions, driving phase separation with centrifugation. Phase separation was identified by monitoring the quench indicating parameter, measured using an external Compton source. Samples were also characterized by dynamic light scattering, where in an extreme case, phase separation could be observed in real time. We describe a stable cocktail with 0.01 mass fraction added Li, a relatively high Li concentration.

Keywords

Phase separation; inverse beta decay; neutrino; neutron; liquid scintillation; Li-6

Introduction

Neutrino detection for measuring reactor antineutrino flux and spectra is an area of intense study. Reactor antineutrino anomalies have been interpreted to indicate that a non-Standard Model neutrino may exist, the sterile neutrino [1–3], although the experimental and theoretical situation is far from clear [4]. As additional short-to-very-short baseline antineutrino experiments are ramping up to address this situation [e.g., 5,6,7], knowing the signal stability and detection efficiency of these experiments is essential.

Although different methods exist, neutrinos can be detected through liquid scintillation (LS) detection—often using scintillants doped with B, Gd, or Li that promote neutron capture [1,8–10]. Neutrino detection relies on inverse β -decay:

$$\bar{\nu}_e + p \rightarrow e^+ + n \quad (1)$$

so that a proton-rich target is desired. The organic solvents typically used in liquid scintillants suffice in this regard. The positron emitted in inverse β -decay is detected by LS

with high efficiency. Doped scintillants achieve improved detection efficiency by generating scintillation light from the neutron capture as well, e.g.,

Here, the emitted α particle is detected by LS with high efficiency [9]. In a scintillant that allows for good α/β discrimination, backgrounds can be reduced by applying a delayed or gated coincidence routine.

Although commercially available Li-doped scintillants were available in the past, currently researchers must load Li into scintillants themselves; the procedure involves adding aqueous LiCl solution to surfactant-containing organic cocktails (these are often commercially available) to form stable microemulsions, also called reverse micellar solutions [8,9,11].

Incorrect proportions of dopant-to-scintillant can result in a thermodynamically unstable emulsion with constituents that will separate with time. This is most common when the aqueous mass fraction (f_{aq}) is too high. Neutrino detection efficiencies are low and, therefore, require extended counting times to obtain sufficient counting statistics; an unstable emulsion can distort or disrupt a long-running experiment [1].

Here, we explore the delicate balance between maximizing ${}^6\text{Li}$ concentration to promote neutron capture while preserving the long-term stability afforded by a true microemulsion. We artificially “age” some samples by centrifugation, identifying emulsions that, on shorter timescales, masquerade as microemulsions. Since phase separation is a process driven by gravity because of differences in the relative densities of the separating components, it was thought that increasing the “gravity” experienced by the samples might effectively provide means of accelerated “aging”. We describe a formulation with approximately 1 % Li by mass that appears to be thermodynamically stable and may provide an easily prepared, inexpensive cocktail for neutrino and neutron detection.

Methodology

Aqueous LiCl solutions were prepared by diluting an $8\text{ mol}\cdot\text{L}^{-1}$ (Sigma Aldrich, St. Louis, MO; used as delivered without further purification)¹ solution which was of natural isotope composition (approximately 0.076 mole fraction ${}^6\text{Li}$ and 0.924 mole fraction ${}^7\text{Li}$ [12]). Diluted and undiluted solutions were added volumetrically to several scintillants to identify optimal loading conditions. Initial studies indicated that the Ultima Gold AB cocktail (UGAB; PerkinElmer, Waltham, MA) could accommodate relatively high concentrations of the undiluted $8\text{ mol}\cdot\text{L}^{-1}$ LiCl solution, and so this promising combination of scintillant and concentrated aqueous LiCl is the focus of the work described herein. UGAB is a diisopropyl naphthalene-based scintillant containing several surfactants, including

¹Certain commercial equipment, instruments, or materials are identified in this paper to foster understanding. Such identification does not imply recommendation by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

nonylphenol polyethoxylates. Samples were agitated by hand to mix the aqueous LiCl into the cocktail.

Two matched series of 5 UGAB samples each with Li mass fractions ranging from 0.005 to 0.025 and total volume of 10 mL were prepared in 20 mL glass LS vials. Quench indicating parameters (QIPs) were measured on a Beckman Coulter LS6500 (Beckman Coulter, Fullerton, CA) liquid scintillation counter equipped with a ^{137}Cs source to generate the Compton spectrum used to characterize quenching. The Beckman counter reports the QIP in terms of the Horrock's number (H#), which is defined as the inflection point at the Compton edge [14]. Repeated measurements over time revealed phase instability in some samples. One week after the initial preparation, one set of samples was subjected to centrifugation at 43 s^{-1} for 8 h. Following the centrifugation step, QIPs were measured again for all samples.

Another identical series of Li-loaded UGAB samples was prepared and the samples were measured by dynamic light scattering (DLS) on a Zetasizer Nano ZS (Malvern Instruments, Inc., Wetborough, MA). For comparison, a set of UGAB samples was prepared by adding distilled deionized water to achieve total aqueous fractions matching the Li-loaded series. All DLS measurements were performed in acrylic cuvettes at $25\text{ }^{\circ}\text{C}$ using the protocols and input data described previously [13]. Each sample was measured three times with 10 runs per measurement and 10 s per run. The hydrodynamic diameters (HD) and polydispersity indices (PI) generated by the instrument software were recorded for each measurement.

Results and discussion

Figure 1 shows the measured QIPs as a function of time elapsed since sample preparation. The sample with, $f_{\text{Li}} = 0.025$ (where f_{Li} is the Li mass fraction, defined as the mass of Li divided by the total sample mass) exhibits a very sharp drop in quenching within a few hours of its initial preparation. This is a clear example of an unstable emulsion undergoing phase separation. The other samples exhibit stable QIPs until centrifugation (about a week after preparation). The sample with $f_{\text{Li}} = 0.015$ shows a sharp drop in quenching upon centrifugation; the matched control (i.e., not centrifuged) sample maintains its original QIP. This result clearly shows how an emulsion can masquerade as a thermodynamically stable microemulsion for relatively long periods of time (in this case, >20 days, Fig. 1). The remaining samples, with $f_{\text{Li}} \leq 0.010$, show no signs of phase separation.

Figure 2 shows the results of the DLS measurements. To ease comparison of the Li- and water-loaded samples, the aqueous fraction, f_{aq} (mass of aqueous material / total sample mass), is shown. The HD measurements (Figure 2a) indicate that the reverse micelles in the Li-loaded series are generally larger than those in the cocktails prepared with UGAB and pure water. It also appears that the size of the reverse micelles increases more rapidly with the addition of $8\text{ mol}\cdot\text{L}^{-1}$ LiCl than with water. For the sample with $f_{\text{Li}} = 0.025$ ($f_{\text{aq}} = 0.46$), the initial set of three measurements showed larger-than-typical dispersion and a pronounced trend with time. So, more measurements were taken (Figure 2b). Over a period of $\approx 30\text{ min.}$, the measured HD increased from 14.4 nm to 18.9 nm. This is interpreted as indicating the agglomeration of aqueous domains, a first step in the phase separation of the unstable emulsion.

Except for the sample with $f_{Li} = 0.025$, the PI measurements (Figure 2c-d) showed little difference in the polydispersity of the reverse micelles in the Li- and water-loaded samples. Figure 2d shows that the increasing average HD observed over 30 min. in the $f_{Li} = 0.025$ sample is accompanied by increasing PI.

Operating on the shorter timescale, the DLS experiments do not detect phase instability in the sample with $f_{Li} = 0.015$; for that sample, instability is only evident after centrifugation.

The data presented here show that it is possible to stably load a readily available organic liquid scintillant, Ultima Gold AB, with a Li mass fraction up to 0.01. As Table 1 shows, this Li concentration is much higher than in other recently reported scintillation cocktails. A higher level of Li gives the advantage of better neutron detection efficiency. But as the total aqueous fraction in the cocktail increases, so does the overall quenching (see increasing H# with increasing f_{Li} in Figure 1). So, neutron capture efficiency must be balanced with total light yield in order to find an optimal cocktail formulation. Further work with Ultima Gold AB-based and other cocktails is planned.

Conclusions

We observed phase separation by monitoring QIPs and demonstrated that phase separation in apparently stable formulations can be driven by centrifugation. Using this approach, we can more confidently predict long-term stability for specific formulations. We describe a cocktail loaded with 1 % Li by mass that performs well in these stability tests. This Li concentration is much higher than in other scintillation cocktails recently described in the literature.

We observed nascent phase separation in real time via DLS, seeing signs of reverse micelle agglomeration accompanied by increasing polydispersity.

Applying these techniques will help us to design optimally loaded scintillation cocktails for future study. We can confidently weed out candidates that will be unsuitable for longer-term applications. We are currently deploying a UGAB-based cocktail loaded with 0.008 Li mass fraction in a neutron spectrometer at NIST, and we hope to report soon on more characteristics of this promising formulation.

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Fig. 1.

Quench indicating parameter measurements in terms of the Horrock's number (H#) for the series of Li-loaded UGAB cocktails as a function of time. The 8 h centrifugation occurred approximately 7 d after sample preparation; centrifuged samples are shown with circles and solid lines (blue) while control samples are shown with triangles and dashed lines (red). The Li mass fraction, f_{Li} (mass of Li / total sample mass) is given in each panel.

Fig. 2. Dynamic light scattering (DLS) results. Measured (A) hydrodynamic diameters (HD) and (C) polydispersity indices (PI) as a function of aqueous fraction. Measured (B) HD and (D) PI for the sample with indicating parameter indicating parameter water and open circles represent those prepared with 8 mol·L⁻¹ LiCl.

Table 1:

Comparison of Li Loading of similar Li-doped LSC experiments

Work	citation number	Li mass fraction [*]	H/C [†]
<i>this work</i>	-	0.010	1.51
Bass et al., 2013	[8]	0.004	1.57
Fisher et al., 2011	[9]	0.0015	1.5
Aleksan et al., 1989	[15]	0.0015	nr
Tanaka and Watanabe 2014	[16]	0.0015	nr

^{*} generally reported as ⁶Li—in the present work, ^{nat}Li was used, so that the equivalent mole fraction with ⁶Li corresponds to a mass fraction of 0.0087.

[†] H/C is the hydrogen-to-carbon ratio; non-reported data listed as “nr”