Micellar phase boundaries under the influence of ethyl alcohol

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HIGHLIGHTS

- Compton spectrum quenching technique applied to find micellar phase boundaries.
- Toluenic Triton X-100 and Ultima Gold AB investigated.
- Ethyl alcohol affects phase boundaries in Triton X-100, not in Ultima Gold AB.
- Phase boundary observations discussed in terms of relevant molecular interactions.

ARTICLE INFO

ABSTRACT

The Compton spectrum quenching technique is used to monitor the effect of ethyl alcohol (EtOH) additions on phase boundaries in two systems. In toluenic solutions of the nonionic surfactant, Triton X-100, EtOH shifts the boundary separating the first clear phase from the first turbid phase to higher water:surfactant ratios. In a commonly used scintillant, Ultima Gold AB, the critical micelle concentration is not shifted. The molecular interactions behind the observations and implications for liquid scintillation counting are discussed.

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1. Introduction

In liquid scintillation counting (LSC), the emission of electrons or α-particles by a decaying radionuclide results in the deposition of energy into a scintillant which converts that energy to visible light for detection. Models for calculating the efficiency with which radionuclidic decays result in optical photons are essential to metrological applications of LSC, and their sophistication has been steadily increasing (Broda et al., 2007; Grau Carles, 2007; Kossert and Grau Carles, 2008, 2010; Kossert et al., 2014). Once optical photons are produced in a scintillant (with a specific "scintillation efficiency"), their transmission to and detection by the photomultiplier tubes defines the "detection efficiency". To a simple first approximation, the "counting efficiency" calculated in metrological models can be considered a product of these two efficiency components.

Because most radionuclides of interest are found in aqueous solutions, the problem of accommodating an aqueous sample in an organic scintillant arises. This problem is met by the addition of surfactants to the organic scintillants so that the aqueous material may reside in reverse micelles. Any given scintillant has a characteristic "loading capacity", and it is often obvious when a given composition is unsatisfactory; emulsification, resulting in a cloudy or opaque suspension, is visually obvious and ultimately results in phase separation (which is also visually obvious). Good compositions result in samples that are visually clear.

Even "clear" LSC samples can have very different micellar—and therefore optical—properties. A series of dynamic light scattering measurements (Bergeron, 2012) identified an apparent critical micelle concentration (cmc) in the commonly used commercial scintillant, Ultima Gold AB (UGAB; PerkinElmer, Waltham, MA, USA),[1] at an aqueous fraction (*f*) of approximately 5% (by volume). Measurements using a Compton spectrum quenching (CSQ) technique—much more convenient than dynamic light scattering in the contexts of an LSC experiment—confirmed the cmc in UGAB, finding it at *f*=0.034(3) (Bergeron, 2014). It was further pointed

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[1] Certain 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.

out that the cmc in UGAB might explain a bias observed in the LSC standardization of ^{63}Ni; Zimmerman and Collé (1997) found that activities recovered from samples with $f < 0.05$ returned activities 1.4% lower than samples with $f > 0.05$. The conclusion offered by Zimmerman and Collé (1997), and repeated by Bergeron (2012, 2014), was that UGAB should be used with $f > 0.05$. In order to avoid unwanted optical complications in LSC measurements, it is wise to avoid sample compositions that might fall near the cmc.

To avoid the cmc, it might help to be wary of chemical additives that could move the cmc. That alcohols acting as cosolvents or cosurfactants affect cmcs in micellar solutions is well-known (Kumar and Balasubramanian, 1979; Bayrak and Iscan, 2005; Bielawska et al., 2013, 2014, 2015; Gu and Galera-Gómez, 1999; Kaushik et al., 2007; Nazir et al., 2009; Zana, 1994, 1995). As co-surfactants, alcohols can be selected to substantially increase the water loading capacity of solutions with surfactants in organic solvents, increasing micellar diameters while often reducing polydispersity. As cosolvents, alcohols can reduce strain at the micellar interface, mediating the hydrophilic interactions that drive surfactant aggregation and reverse micelle formation. Longer chain alcohols, more soluble in apolar solvents, tend to behave as cosurfactants to higher concentrations. Shorter chain alcohols, such as ethyl alcohol (EtOH) can act as cosurfactants at low concentrations, but tend to act as cosolvents at higher concentrations. Depending on the molecular dynamics of the specific system, EtOH might increase or decrease a cmc. To further complicate the matter, cmcs in reverse micellar systems (microemulsions) are generally thought to correspond more to a range than to a precise singular value; the phase boundary is a complex region of the tertiary phase diagram with a dynamic equilibrium between reverse micelles and premicellar aggregates. The addition of an alcohol acting as a cosurfactant or cosolvent may therefore move the cmc or narrow or broaden the range over which the complex dynamic equilibrium corresponding to the cmc occurs.

A concern over the use of ethanolic nitromethane (NM) as a quenching agent in LSC experiments was very recently raised (Bergeron, 2014). In many LSC experiments, the efficiency model is tested by performing measurements on a series of differently quenched samples, creating a "quench curve". A good model of the counting efficiency as a function of quenching will return the same activity for each of the differently quenched samples. Thus, the concern with ethanolic NM was that if EtOH affects the phase boundary, then a series of samples with different amounts of EtOH may include samples with optical properties not anticipated in a model relying on a single quench curve.

In this work, that concern is addressed. Small amounts of EtOH, consistent with the additions typical in LSC experiments, are added to UGAB samples and the CSQ technique is used to monitor cmcs. Samples with the nonionic surfactant, Triton X-100 (TX-100; Sigma Aldrich, St. Louis, MO, USA), in toluene are also studied using the same methodology. As much as possible, the observed cmc effects are discussed in terms of relevant molecular interactions.

2. Experiment

The Compton spectrum quenching (CSQ) technique for determining micellar phase boundaries (Bergeron, 2014) was applied to several series of samples prepared with the scintillant Ultima Gold AB (UGAB) and with toluenic solutions of the nonionic surfactant, Triton X-100 (TX-100).

2.1. Sample preparation

The EtOH concentrations in the different series were selected to correspond to the addition of 2 or 14 "drops". The idea was to cover the full range of EtOH concentrations likely to arise in a LSC experiment with efficiency variation, where we often prepare a series with 2–14 drops of 1:10 NM:EtOH.

Two experiments were performed with toluenic Triton X-100 solutions. In the first, a solution of Triton X-100 with a mass fraction of 26.1% was prepared gravimetrically. This solution was used to volumetrically prepare 45 samples (3 series of 15 samples, each containing nominally 10 mL of the Triton X-100 solution) with dispensettes and micropipettes. Then, EtOH (0 mL, 0.030 mL, or 0.280 mL, depending on the series) and water additions (0.013 mL to 0.588 mL) were made volumetrically to each sample individually.

In the second experiment with toluenic Triton X-100, a solution with a 29.2% mass fraction was prepared gravimetrically. This solution was then used to prepare two additional "master" solutions with added EtOH mass fractions of 0.3% and 2.5%. Each of the three master solutions was used to prepare a series with 16 samples, to which 0.014 g to 0.732 g of water was added, resulting in a range for the molar fraction of water to TX-100 of $\omega_{0,T} = 0.20$ to 10.45.

The UGAB series were prepared volumetrically with dispensettes and micropipettes, consistent with the procedures used in the first TX-100 experiment. Aqueous mass fractions, f, were calculated from the standard densities of the volumetrically added components. For these series, 10 mL of UGAB was added to each of 52 20 mL scintillation vials for 4 series of 13 samples each. EtOH was then added to each sample individually (0 mL, 0.030 mL, 0.105 mL, or 0.280 mL). Then, 0.05 mL to 1.14 mL of deionized distilled water was added to achieve a range of values for f.

2.2. QIP measurements

After agitation and visual inspection for turbidity or phase separation, samples were counted on a Beckman Coulter LS6500 (Beckman Coulter, Fullerton, CA, USA) liquid scintillation counter. The Beckman counter is equipped with an internal ^{137}Cs source to produce Compton electrons in a sample. The Compton spectrum is analyzed by system software, taking the inflection point at the Compton edge as the Horrock's number (H#) as a measure of quenching. This quench indicating parameter (QIP) can be used to identify micellar phase boundaries in UGAB and TX-100 samples (Bergeron, 2014). This QIP increases with increasing water content, with the slope of the curve exhibiting a change at or near the phase boundary. So, calculating the intersection of two linear fits gives a value for the concentration where the phase boundary occurs. This technique can be very sensitive to the somewhat arbitrary binning of data as belonging to one or the other curve, as was discussed previously in terms of the "data attribution sensitivity" (DAS) uncertainty (Bergeron, 2014). DAS can be assessed by performing the analysis with multiple attribution schemes, as has been done here.

3. Results

The QIP data were used to determine the effect of added EtOH on phase boundaries in TX-100 and UGAB samples.

3.1. TX-100

The presence of phase boundaries in the toluene/TX-100/water system is visibly apparent in the onset of a turbid phase at $\omega_{0,T} \approx 0.7$, persisting to $\omega_{0,T} \approx 5$. The region below $\omega_{0,T} \approx 0.7$ is thought to correspond to individual water molecules associated with TX-100 molecules; the region above $\omega_{0,T} \approx 5$ is the reverse micellar phase (Rodríguez et al., 1998; Bergeron, 2012; Bergeron, 2014). In