Micellar phase boundaries under the influence of ethyl alcohol

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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.

Keywords: liquid scintillation counting; critical micelle concentration; ethanol; cocktail; microemulsion; reverse micelle

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 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 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, M. et al., 2013; 2014; 2015; Gu and Galera-Gómez, 1999; Kaushik, et al., 2007; Nazir, et al., 2009; Zana, 1994; 1995). As cosurfactants, 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

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.

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 to 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 the present studies, we inspected the samples visually, looking for the first sign of clouding that indicates the onset of the turbid phase and for the complete clearing of the turbid phase that indicates complete micellization. Table 1 summarizes these observations. These numbers are based on subjective judgments of clarity, and so it is not too surprising that the observed ranges for the phase boundaries are not perfectly consistent between the two experiments.

The QIP results for the agitated samples are presented in Figure 1a. The uncertainty bars represent the standard deviation on three repeated cycles. Turbid samples prone to phase separation therefore typically have larger uncertainty bars. EtOH acts as a quencher, with the series to which EtOH has been added having consistently higher H# than the series with toluenic TX-100 and water only.

The QIP data were binned using five to six different attribution schemes in order to calculate intersects corresponding to the boundary separating the first clear phase from the turbid phase. The intersects calculated with the different attribution schemes were averaged and the standard deviation on the values used for the average was taken as the DAS uncertainty. The DAS uncertainty was combined in quadrature with the average standard fit uncertainty and with an estimated weighing uncertainty to calculate a combined standard uncertainty. Figure 1b plots the average intersect values with their appropriate standard uncertainties and shows that the data indicate that the phase boundary shifts to higher $\omega_{0,T}$ with the addition of $\approx 3\%$ EtOH.

In Figure 1b and throughout this work, uncertainties are given as combined standard uncertainties ($k = 1$), calculated as the quadratic sum of individual uncertainty components.

3.2. UGAB results

The phase boundary in our UGAB samples does not involve a turbid phase and so cannot be seen by visual sample inspection. QIP results are presented in Figure 2a. The data were taken over four days, with three runs of 10 cycles each. The standard deviation on 10 measurements is reflected in the uncertainty bars in Figure 2a. The uncertainty bars are mostly smaller than the symbols, and the symbols for the different runs are indistinguishable. Here again, there is evidence that EtOH acts as a quencher.

The QIP data were binned into five different attribution schemes in order to calculate intersects corresponding to the UGAB cmc. The intersects and DAS uncertainty were calculated as for the TX-100 samples. Figure 2b plots the average intersect values with their appropriate standard

uncertainties and shows that the data indicate no clear trend in the cmc with the addition of ≈ 3 % EtOH.

4. Discussion

4.1. Quenching by EtOH

Figures 1a and 2a show that EtOH acts as a quenching agent in both toluenic TX-100 and UGAB. We are interested in the effect EtOH has in LSC experiments, since it is often used as the carrier for the chemical quenching agent, nitromethane (NM). NM acts as an electron acceptor, offering a non-radiative relaxation pathway for excited fluor molecules (see, for example, Breymann, et al., 1978). EtOH may act as a much weaker electron acceptor, and a recent study Braem, et al. (2012) has provided some insight on the precise molecular mechanism by which a polar alcohol may affect the fluorescence of a fluor such as 2,5-diphenyloxazole (PPO; the fluor found in most commercial scintillants, including UGAB). They found that a polar solvent interacts with the oxygen and nitrogen atoms on the PPO oxazole moiety (see Figure 3), damping out of plane distortions and affecting the excited state structure. In an apolar solvent, the excited state structure is quite different from the ground state structure, so that the slow intramolecular vibrational redistribution and vibrational energy transfer to the solvent define the relaxation dynamics. Braem, et al. (2012) observed that the relaxation dynamics were much faster in EtOH than in cyclohexane, indicating that the excited state structure in the polar solvent is closer to the ground state structure, consistent with the increased symmetry in the static excitation/emission spectra. The result is a change in the Franck-Condon factors with increased solvent polarity. In UGAB, the situation is complicated by the “secondary” fluor, 1,4-bis(methylstyryl)-benzene.

To confirm that the presence of EtOH affects the vibronic structure in the anticipated manner, we prepared TX-100 and UGAB solutions with and without 30 % EtOH added. In static fluorescence spectra, the excitation and emission spectra of TX-100 and UGAB samples are blueshifted slightly with the addition of EtOH.

The observed quenching effects (Figures 1a and 2a) likely result from the energetic shifting or (de)population of modes that typically couple to excited solvent molecules or chemical quenchers (such as triplet oxygen). Interestingly, fluors that participate in hydrogen bonding interactions with EtOH are known to exhibit decreased quenching by electron acceptor molecules (Ahmad and Durocher, 1981).

The concentration of dissolved oxygen should not be expected to increase with EtOH addition since oxygen is more soluble in aromatic organic solvents than in EtOH (Battino, et al., 1983).

EtOH is a weaker quencher than NM. The question in LSC becomes whether the quenching mechanisms are different enough that a series of samples quenched by addition of 1:10 NM:EtOH should not be considered describable with a one-variable model for quenching. In other words, do the samples lie on the same quench curve? For most LSC experiments, the quench curves will be close enough together so as to be indistinguishable. We cannot presently say whether problems that arise with “difficult” nuclides, including those that emit low-energy Auger electrons, might be partially due to subtle quenching effects from two-component quenchers.

4.2. Effect of EtOH addition on phase boundary

4.2.1. TX-100

The phase boundaries determined using the CSQ method were consistent with previous results. For the TX-100 samples with no added EtOH, the analysis of intersects implied a phase boundary at $\omega_{0,T} = 0.75(18)$. The corresponding value in the 2014 report was $\omega_{0,T} = 0.65(1)$, where the uncertainty does not include a component for DAS. Using the average DAS uncertainty (24.7 %) from the current studies, the 2014 phase boundary was recalculated as $\omega_{0,T} = 0.65(16)$. All of these results are consistent with the observations of Rodríguez, et al. (1998), who reported a phase boundary for toluenic TX-100 at $\omega_{0,T} = 0.6$.

Figure 1b reflects the change in the phase boundary in the toluenic TX-100 system with the addition of EtOH. The boundary (i.e., “intersect” in Figure 1b) appears to drop to slightly lower $\omega_{0,T}$ with the addition of 0.3 % EtOH. The drop observed here is within the uncertainty, and could easily be dismissed. It is, however, consistent with observations on aqueous TX-100 where the cmc was observed to decrease slightly with increasing EtOH concentration in the bulk phase up to approximately $0.5 \text{ mol}\cdot\text{L}^{-1}$ (≈ 2.3 % mass fraction), increasing steadily thereafter with higher EtOH concentrations (Bielawska, et al., 2013). The initial drop in the aqueous sample was explained in terms of EtOH molecules replacing water molecules on the oxyethylene groups of the surfactant, thus decreasing the repulsive forces between proximate hydrophobic chains and promoting micellization. It may be that a similar mechanism of interaction plays out in toluene.

While the dip in the curve in Figure 1b at 0.3 % EtOH may or may not be real, the rise at 3 % EtOH seems more certain. Again, this is consistent with observations on the aqueous system (Bielawska, et al., 2013), where increased cmc is attributed to decreased entropic cost of micellization. Dissolving an alcohol in water disrupts the extended hydrogen bond network at an enthalpic and entropic cost. Micellization similarly has an entropic cost, but that cost is reduced in the presence of the alcohol since the hydrogen bond network is already disrupted.

Clearly, the aggregation mechanisms in toluene are different than in water. The role that EtOH plays in the formation of reverse micelles does not involve disruptions to the hydrogen bond network of the solvent; there isn't one. When EtOH partitions to the toluenic phase, the polarity of the solvent is increased. Following Zana (1994; 1995), we can understand the effect on aggregation in terms of interfacial strain. The increased polarity of the solvent results in a decreased hydrophobic response from the surfactant. Interfacial strain is reduced, the tendency towards curvature is reduced, and the pre-aggregation (clear) phase persists to higher $\omega_{0,T}$.

At the molecular level, it is also possible that EtOH interactions at the oxyethylene groups (see Figure 3) may inhibit rotational freedom along the TX-100 chains, thus decreasing the entropy of the toluenic solution. Thus, as in the aqueous case, the entropic cost of micellization is reduced because the dissolution of EtOH has already resulted in decreased entropy. Further, we expect that as water displaces EtOH molecules interacting with the -OH termini of TX-100 molecules, more EtOH would tend to interact with the oxyethylene groups, amplifying the entropic effect.

In terms of molar ratios, the 0.3 % EtOH samples have an EtOH:TX-100 ratio of 0.046:1. For the 3 % EtOH samples, the ratio is 0.46:1. So, in all of the samples in this work the surfactant molecules outnumber the EtOH molecules by a wide margin, bringing the validity of the cosolvent model into question. But EtOH is quite soluble in toluene without TX-100 (Skrzecz, et al., 1999), and in our studies it is clear that the phase boundaries we recover are not constant in terms of a combined molar ratio of the sum of EtOH and water to TX-100. So, EtOH should not be considered a cosolute.

As a cosurfactant, we return to the molecular interactions between EtOH and the TX-100-water complexes. Here we would try to argue that EtOH might help stabilize the premicellar moieties by forming hydrogen bonds with the water molecules (which are, in turn, participating in a hydrogen bonding interaction with the –OH termini of TX-100 molecules). If the dip in Figure 1b is real, then it seems that molecular interactions between EtOH and TX-100 do not stabilize the premicellar phase, but actually promote micellization. So, the cosurfactant explanation for EtOH pushing the phase boundary to higher $\omega_{0,T}$ is only valid if the dip is not real. Overall, the cosolvent model provides the best explanation of the 3 % EtOH data point in Figure 1b. Certainly, cosolvent-type effects are expected to dominate with higher EtOH concentrations.

4.2.2. UGAB

For the UGAB samples with no added EtOH, the analysis of intersects implied a phase boundary at $f = 0.029(6)$. The corresponding value in the 2014 report was $f = 0.034(2)$, where the uncertainty does not include a component for DAS. Again, using the average DAS uncertainty (11.3 %) from the current UGAB studies, the 2014 phase boundary was recalculated as $f =$

0.034(4). As discussed in the 2014 report, CSQ results place the phase boundary slightly lower than DLS experiments (Bergeron 2012), probably indicating that the phase transition is fairly gradual.

Figure 2b shows that the micellar phase boundary in UGAB does not change significantly with the addition of EtOH. Because the exact composition of UGAB is proprietary (and has unknown batch-to-batch variability), it is difficult to comment on the molecular dynamics of the system without resorting to conjecture. The manufacturer-provided material safety data sheet (MSDS) at least provides a reasonable launching point for said conjecture.

The solvent for UGAB is diisopropyl naphthalene (CAS: 38640-62-9; DINN) and accounts for “40 % to 60 %” of the formulation. Alkylphenol polyglycoethers (CAS: 9016-45-9), also referred to as nonyphenol ethoxylates (NPEs), account for “22.5 % to 50 %”, and 2-(2-butoxyethoxy)ethanol (CAS: 112-34-5), also referred to as butyl diglycol (BDG), accounts for another “10 % to 20 %”. These latter two components are the nonionic surfactants that give UGAB its high aqueous loading capacity. The fluor and wavelength shifter are not particularly important to understanding the micellization dynamics.

DINN is much less polar than toluene. We therefore expect that when the molar ratio of EtOH to surfactants is less than 1, which is definitely the case in the present studies, EtOH molecules will tend to associate with surfactant molecules. NPEs and BDG have the same type of oxyethylene moieties as TX-100 (see Figure 3), and so the possible association of EtOH molecules along the chain might inhibit rotational freedom, decreasing entropy as described in the preceding section.

In addition, the types of chemistry expected at the –OH terminus of TX-100 would also be expected at NPE and BDG termini.

The reason that we do not see an effect of EtOH concentration on the cmc in UGAB is probably that the surfactant concentrations are much higher. Thus the effective $\omega_{0,T}$ for the same f is much lower. It is possible that the cmc could be observed to shift with much higher concentrations of EtOH, but those would not be expected to be relevant in a LSC experiment. The concern that addition of ethanolic nitromethane as a quenching agent might affect the value of f corresponding to the cmc (Bergeron, 2014) is rejected.

4.3. Adsorption

Turbid TX-100 samples ultimately phase separated, as expected of an emulsion. In a subset of samples, particularly those near the phase boundary separating the first clear phase from the turbid phase, it appeared that some of the phase-separated material could not be re-suspended. This was attributed to adsorption of surfactant to the vial surface. In some systems, micellization has been shown to affect surfactant adsorption kinetics, with a sharp increase in adsorption density near the cmc; the presence of alcohols in surfactant systems can also have a strong effect on the adsorption kinetics (Blokhus, 1990; Sjöblom, et al., 1990; Zana, 1995). We did not observe any differences in the irreversible adsorption between the series with and without EtOH, and were unable to find any examples in the literature of EtOH impacting surfactant adsorption kinetics. Further, we did not observe irreversible adsorption in any of the UGAB samples.

5. Conclusions

Ethyl alcohol (EtOH) acts as a quenching agent in Ultima Gold AB (UGAB) and toluenic Triton X-100 (TX-100). Some of the molecular interactions involved in its quenching behavior were discussed, but it remains unclear whether the overall mechanism is sufficiently different from that of NM to jeopardize the validity of the one-quench-curve assumption in LSC experiments using ethanolic nitromethane. In the future, this question can be probed by measuring, for example, ^3H efficiency as a function of QIP in two sets of NM-quenched samples with and without matching of the total EtOH volume.

EtOH can affect micellar phase boundaries. We observed a change in the ratio of water:surfactant ($\omega_{0,T}$) defining the transition from the first clear phase to the first turbid phase in TX-100 solutions. The surfactant concentration in UGAB is high enough that the EtOH additions in a typical LSC experiment will not at all affect the micellar phase boundary. Therefore, they will not impact the optical properties of the system. It is still important to select cocktail compositions with aqueous fractions relatively far from the cmc (≈ 0.03 to 0.05).

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Table 1 Visual identification of the onset and disappearance turbidity in toluenic TX-100

samples in the first (E1) and second (E2) experiments. All values are given in terms of $\omega_{0,T}$.

	last clear	first turbid	last turbid	first clear
E1 - no EtOH	0.60	0.70	2.98	4.98
E1 - 0.3 % EtOH	0.65	0.75	3.03	5.02
E1 - 3.0 % EtOH	1.46	1.72	5.46	7.40
E2 - no EtOH	0.94	2.67	4.86	6.78
E2 - 0.3 % EtOH	0.69	0.79	3.91	4.90
E2 - 3.0 % EtOH	1.04	1.15	5.39	6.40

Figure 1 (a) QIP measurements on TX-100 samples with and without added EtOH. Uncertainty bars correspond to the standard deviation on three determinations. Dashed lines are meant only to guide the eye. (b) Micellar phase boundaries calculated from the intersects of fits to the QIP data. Uncertainty bars correspond to standard combined uncertainties (see text).

Figure 2 (a) QIP measurements on UGAB samples with and without added EtOH. Uncertainty bars correspond to the standard deviation on ten determinations. (b) Critical micelle concentrations calculated from the intersects of fits to the QIP data. Uncertainty bars correspond to standard combined uncertainties (see text).

Figure 3 Structures for some of the molecules discussed in the text. Note that for DINN and NPE only one isomeric form is depicted. In general, scintillants can be expected to host a mix of isomers.