On the reverse micelle effect in liquid scintillation counting

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ABSTRACT

This work looks into the tracks of electrons in nanoemulsive scintillating media using the Monte Carlo Geant4-DNA code which simulates event-by-event interactions of electrons in liquid water down to the eV, without resorting to the condensed history method. It demonstrates that the average number of micelles in which electrons deposit energy is quite large, increasing with their emission energy, decreasing with micelle size, and rising with micelle concentration. The probability of an electron ending its track in a micelle is found to be rather large and micelle size-dependent below 1 keV, and approximating the aqueous fraction at higher energies. Analyses of the Monte Carlo estimated energy depositions in the aqueous phase and in the scintillant tell of a micelle quenching effect, with the micelle size shaping the quenching at low energy and the micelle concentration governing it at higher energies. The micelle effect on the ^{3}H and ^{63}Ni beta spectra is discussed for a range of micelle sizes and concentrations. This paper also computes the ionisation quenching function using Birk's law whilst considering the full energy losses in the micelles bisecting the electron pathway, and not just that incurred in the primary micelle enclosing the decaying nuclide. The ionisation quenching function is then used to calculate the detection efficiencies for ^{3}H, ^{63}Ni, ^{54}Mn and ^{55}Fe. The effect of the micelle size is found to be small for beta emitters but significant for the electron capture nuclides. TDCR measurements of ^{63}Ni samples covering 8 aqueous fractions are analysed with and without explicit treatment of the micelle effect. Activities in the two representations agree within 0.02%. The ratios of the corresponding figures of merit are found to coincide with the scintillant fractions.

1. Introduction

Sample preparation for liquid scintillation analysis often involves dissolving radioactive solutions into organic liquid scintillation cocktails. Since most radioisotopes are available in aqueous form, which is not miscible with the aromatic solvents of the cocktails, surfactants are used to increase the interface between the aqueous phase and the organic one. This stable dispersion of aqueous droplets – reverse micelles of nanometric size – in the continuous organic medium may be regarded as a nanoemulsion (Anton and Vandamme, 2011).

The nanoemulsive nature of samples in liquid scintillation counting has been the focus of increased interest in recent years. Several works were published on the effects of the reverse micelle size on the liquid scintillation detection efficiency (Grau Carles, 2007a, 2007b; Kossert and Grau Carles, 2010; Bergeron and Laureano-Perez, 2014) and efforts were made to determine experimentally the sizes of reverse micelles in commonly used commercial liquid scintillation cocktails (Kaushik et al., 2006; Bergeron, 2012; Nedjadi et al., 2016).

Using dynamic light scattering, Bergeron measured the sizes of the reverse micelles – henceforth denoted as micelles, for short – in eight

commercial scintillants and found them to be smaller than the then widely used 8 nm diameter (Bergeron, 2012). In addition, Bergeron studied the effects of changing the aqueous and acid contents on the micelle sizes. We also measured more recently the diameters of micelles in two scintillants, Ultima Gold and Ultima Gold AB, with the same technique. For Ultima Gold (UG), the micelle diameters were measured to be about 2 nm and slightly dependent of the aqueous fraction, while for Ultima Gold AB (UGAB) they were found to vary strongly with the aqueous fraction and range between 1 and 4 nm. These results agree only partly with the measurements of Bergeron for these two scintillants (Nedjadi et al., 2016).

Knowing the size of micelles in a given sample for liquid scintillation analysis has been deemed important because the electrons, ejected by radioactive decays within a micelle, will lose part of their energy in the aqueous phase before reaching the organic scintillating medium, thus reducing the detection efficiency. Grau Carles initiated the work to account for this efficiency loss, using the results of NOREC Monte Carlo computations of the electron energy depositions inside nanospheres of liquid water (Grau Carles, 2006; Semenenko et al., 2003). He argued that the efficiency loss caused by the micelle size is significant only for

electrons in the 0.1–1 keV energy range, as ionisation quenching renders the effect undetectable for energies below 0.1 keV, while electrons with energies higher than 1 keV 'do not deposit appreciable amount of energy in targets of liquid water of a few nanometers' (Grau Carles, 2007a, 2007b). Thus the prescription he used for accounting for the micelle size effect in the detection efficiency involves correcting the energy available for scintillation, or reduced energy,

$$EQ(E) = \int_0^E \frac{dE'}{1 + kB \cdot \frac{dE'}{dx}} \qquad (1)$$

by replacing E with E–ΔE, where ΔE is the energy deposited within the micelle housing the radioactive decay. ΔE is evaluated as a function of the initial energy of the emitted electron with the NOREC electron track Monte Carlo simulation code (Grau Carles, 2006). The same approach is used in the stochastic models for computing the efficiency (Grau Carles, 2007a, 2007b; Kossert and Grau Carles, 2010). One may call this approach the 'first-micelle correction model' because it accounts only for the electron energy deposited in the original micelle, and it overlooks any subsequent energy depositions in other micelles bisecting the electron pathway.

The starting point of this paper is to question the representation of reality underlying this model. It runs counter to the physical intuition that electrons traverse more micelles than the one from which they originate.

Consider a 20 mL vial, filled with 15 mL of UG into which 45 μL (typically 3 pycnometer drops) of aqueous radioactive solution are deposited. The aqueous fraction, defined here as the ratio between the aqueous sample volume and the scintillant volume, is then 0.3%. Assuming the micelle size distribution is single peaked at 2 nm means the micelle concentration is about 7.2×10^{17} micelles per mL. If we now suppose the micelles are spread uniformly in the organic phase, and that they sit on vertices of elementary cubic cells, then the average intermicellar distance is about 11 nm. Given that the range of say a 10 keV electron is about 2500 nm, i.e. around 250 micelle separations, it is unlikely that such an electron would evade crossing micelles on its track after it leaves the first one. Furthermore, close to the end of its pathway, the energy of the electron drops significantly, below the keV say, and the electron may then traverse micelles or even end its course in one. Such energy depositions are not accounted for by the first-micelle correction model.

Another issue with this model pertains to a basic geometric requirement. Since the aqueous phase is dispersed uniformly in the organic phase, and both media have close densities, one would expect the partitioning of the electron energy between the two phases to reflect on average and to some extent their respective fractions. This should be the case for sufficiently energetic electrons. But in the first-micelle correction model all the energy goes to the organic phase except the bit deposited in the first micelle, regardless of the aqueous fraction involved.

The omission or here incomplete treatment of the electron energy losses in the aqueous phase in the liquid scintillation detection efficiency models seems all the more puzzling because in plastic scintillation with microspheres – where the water-scintillant configuration is reversed – the models require a full account of the energy dissipations in the aqueous phase to obtain meaningful results. (Sanz and Kossert, 2011; Tarancón et al., 2015).

These issues were the motivations to explore quantitatively the reverse micelle effect in liquid scintillation counting using a Monte Carlo simulation of the electron interactions at the nanoscale level. Among the several codes that are available (PARTRAC, NOREC, TRIOL, PITS etc.), we chose the open-source, general purpose Geant4-DNA Monte Carlo simulation toolkit to study the electron tracks structures at the molecular level. This track structure code simulates all the elementary interactions on an event-by-event basis, with no use of condensed history approximations.

This code was used to study the number of micelles crossed as well as the energy depositions in the micelles and in the scintillants, in the case of two cocktails, UG and UGAB, for a range of aqueous fractions used in liquid scintillation radionuclide metrology and for a range of micelle sizes. The code was also used to examine the micelle effects on the beta spectra of tritium and ^{63}Ni. In addition, the electron energy track records into and out of the micelles and the scintillating medium produced by the code were utilised to calculate ionisation quenching functions which take into account all electron energy losses to the aqueous phase. The micelle effect on the detection efficiency in the case of ^{3}H, ^{63}Ni, ^{54}Mn and ^{55}Fe were also estimated. TDCR liquid scintillation measurements of a ^{63}Ni solution were performed as well to probe the micelle effect on the activity concentrations. Analyses of these measurements provide interesting insights into how one may incorporate the aqueous fraction in the traditional efficiency calculation models in liquid scintillation counting.

This work and its main results are described in the remainder of this paper.

2. Method

The Geant4 toolkit (version 4.10.0.1) with the Geant4-DNA low-energy extension was used for this study. This code – indicated as G4DNA hereafter – simulates explicitly the discrete interactions of particles with liquid water without resorting to the condensed history method (Chauvie et al., 2006; Incerti et al., 2010a, 2010b; Bernal et al., 2015). For electrons, the interactions include elastic scattering, ionisation, electronic excitation, vibrational excitations and molecular attachment (Ivanchenko et al., 2012). Electrons are transported down to 7.4 eV, and below this threshold their kinetic energy is deposited locally. For the validation of G4DNA physical processes see Incerti et al. (2010a, 2010b, 2014), Francis et al. (2011), Champion et al. (2014).

The micelles were modelled as nanospheres consisting of just liquid water, neglecting the surfactant molecules which interface the aqueous and organic phases. Furthermore, no distinction is made between the bulk-like water molecules in the core of the micelle and those trapped interfacing with the surfactant molecules (Fayer and Levinger, 2010; Fayer, 2011). The micelles were also assumed to be monodisperse, with their diameter a parameter in the simulations.

Assuming a uniform nanoemulsion, each nanodroplet sits within a 3D cubic simulation box filled with liquid scintillation cocktail (UG or UGAB). Densities of 0.98 and 0.96 g/cm^3 are taken for the water-equivalent UG and UGAB media respectively. The size of this elementary box is determined by the selection of the aqueous fraction and the choice of the micelle size. Simulations were performed with the micelles located randomly within the cubic cells as well as with the micelles in the centres of the lattice, but no significant differences between the two geometries were found. The results reported here are for nanospheres randomly positioned within the simulation box. Although micelles are in a state of Brownian motion, with some of them redistributing their contents through fusions and/or fissions, a static perspective is assumed here, with no micelle collisions and a single size distribution.

Each simulation starts with the water nanosphere randomly placed within a cubic cell. The electron begins its pathway from a random position around the centre of the micelle, and then it is tracked until it reaches the boundary of the box. Periodical boundary conditions are applied in the 3 directions as the box may multiply in any of them. Electron kinematic continuity is enforced at cell boundaries. Tallies are made for the electron energies deposited within micelles and outside them, for the number of micelles crossed, and for the sequences of micelle entrance and exit energies. Most simulations were carried out for 143 initial electron energies between a few eV and 500 keV. Around 10^6 events were simulated for each of these energies. The computations for the micelle effect on the ^{3}H and ^{63}Ni spectra were performed with