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# Ionic liquids as solvents for liquid scintillation technology. Čerenkov counting with 1-Butyl-3-Methylimidazolium Chloride

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## HIGHLIGHTS

- Čerenkov luminescence was detected when $^{18}F$ was dissolved in 1-Butyl-3-Methylimidazolium Chloride (BmimCl) ionic liquid.
- The presence of another type of radiation that could eventually cause coincidences in the photodetectors was safely discarded.
- Čerenkov luminescence serves to determine the activity of a $^{18}F$ solution by means of TDCR–Čerenkov technique.
- Some advantages of the use of BmimCl as solvent for Čerenkov counting were listed.

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## ABSTRACT

We report the detection of the Čerenkov luminescence after the incorporation of a few droplets of a physiological solution of 2-deoxi-2($^{18}F$)fluorine-D-glucose into the ionic liquid 1-Butyl-3-Methylimidazolium Chloride (BmimCl). The phenomenon is attributed to the $\beta^+$ particles having energy above the threshold energy value for the Čerenkov radiation in this medium. The presence of another type of radiation that could eventually cause coincidences in the photodetectors was safely discarded. We show that this property serves to determine the activity of a $^{18}F$ solution by means of the novel TDCR–Čerenkov technique. The results were compared with those obtained from the classic TDCR scintillation method using a commercial scintillation cocktail. The activity values obtained from both methods were found to be virtually identical within the experimental uncertainties. The fact that high energy $\beta$ particles in BmimCl generates Čerenkov photons makes this ionic liquid a promising compound for future research in detection and quantification of ionizing radiation, and it provides a potential alternative for applications in nuclear technology.



## 1. Introduction

The Čerenkov radiation, i.e. the light produced as a charged particle passes through a dielectric medium at a velocity greater than the speed of light in the same medium, has been studied in detail for more than 80 years (Čerenkov, 1937). At the beginning, the analysis of the effects of Čerenkov radiation was restricted to the field of high energetic physics. Only in the 60's, the phenomenon started to be used in liquid scintillation technology, a methodology that involves the detection of the emitted photons coming from a liquid medium, in which a radioactive analyte has been previously dissolved (Rengan, 1983).

Several works in literature have focused attention on how to improve counting efficiency in liquid Čerenkov counters. The use of high refractive index solvents, as a means to decrease the Čerenkov threshold energy (Ross, 1976), and the incorporation of wavelength shifters (Wiebe et al., 1978), are two of the most commonly cited strategies. Although an increment in the refractive index of the solvent does not appear to be significant for activity standardization of high-energy emitters, it becomes relevant for radionuclides emitting $\beta$ particles with energies comparable to the Čerenkov threshold value. For example, the use of a 95% glycerol/water solution – with a refractive index $n=1.46$ – promotes a remarkable one hundred-fold increment in the detection efficiency of $^{99}Tc$ compared to those reported in water (Ross, 1969). Moreover, the coincidence counting efficiency of $^{18}F$ in chlorobutane ($n=1.52$) increases by a factor of two, compared to those reported using dimethyl sulfoxide ($n=1.47$) (Wiebe et al., 1978).

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A good solvent for Čerenkov measurements must fulfill four basic requirements – (a) it should dissolve the analyte of interest; (b) its refractive index should be as high as possible, in order to reduce the threshold energy for Čerenkov photons; (c) it should remain stable against radiation damage; and (d) it should exhibit negligible absorption in the region of emission of Čerenkov photons to prevent a decrease in the counting efficiency as a result of re-absorption phenomena.

In the last 10 years, a new family of compounds, commonly known as ionic liquids, has awakened a great deal of interest in the scientific community. Ionic liquids are room temperature molten salts composed of an organic cation and an inorganic/organic anion (Weingartner, 2008). They have multiple applications in areas such as catalysis (Lombardo et al., 2010), electrochemistry (Silvester et al., 2008), organic synthesis (Castro, 2005), solar cells (Wei et al., 2010), etc. More recently, ionic liquids have also been proposed to be used at different stages of the nuclear fuel cycle (Sun et al., 2011). The large diversity in the choice of the constitutive ions gives rise to the denomination of ILs as "tailored solvents", capable to equally dissolve polar substances, like water, and natural polymers such as cellulose (Pinkert et al., 2009). Due to their scarce volatility, they have been also proposed as a "green" alternative to the most common volatile organic solvents.

At present, a large number of solutions and emulsions are commonly used as solvents in the Čerenkov detection experiments. The choice of a specific scintillation cocktail depends on the characteristics of the sample to be quantified. Aqueous solutions typically exhibit refractive indices comparable to the one of pure water; as such, their use for quantifying radionuclides emitting beta particles with energies near to the Čerenkov threshold in water is rather limited. On the other hand, the use of organic solvents usually present additional problems associated with their toxicity and flammability. Moreover, many emulsions used to suspend water soluble radionuclides, exhibit stability problems associated with the limiting amount of water that they support and the desired prevailing pH. We remark that the homogeneity of the mixture is a key element that guarantees the best counting results. In this context, ionic liquids emerge as new versatile solvents whose thermodynamic characteristics can normally be easily gaged by the nature of their molecular constitution. The strong ionic nature of their intermolecular interactions guarantees minimum evaporation, whereas flammability problems, normally associated to the more common organic phases, are practically absent.

Motivated by the search of new solvents for scintillation technology, in the present work we focus attention on the interaction between β radiation and a particular ionic liquid, 1-Butyl-3-Methylimidazolium Chloride (BmimCl), a viscous and colorless fluid with a relatively high refractive index $n=1.54$. We show that high energy β particles are able to induce the Čerenkov luminescence in this compound and exploit this property to determine the activity of a $^{18}$F solution by means of Čerenkov counting, by using the ionic liquid as solvent in the novel TDCR–Čerenkov method recently developed (Kossert, 2010) which does not requires external samples for calibration.

## 2. Experimental

### 2.1. Chemical treatment and sample preparation

BmimCl was obtained by synthesis in our laboratories following standard procedures (Hallett and Welton, 2011). Freshly distilled 1-chlorobutane (Merck-Reagent for synthesis) was added dropwise to distilled 1-methylimidazole (Merck-Reagent for synthesis) (1.3:1 mol proportion) under vigorous stirring. The mixture was kept at 50 °C for 5 days under continuous stirring, in a $N_2$ atmosphere, and

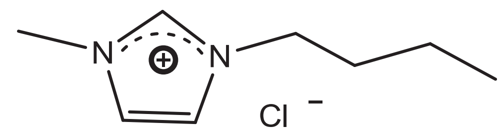


**Chart 1.** Chemical structure of 1-Butyl-3-Methylimidazolium Chloride ionic liquid.

subsequently purified by recrystallization from acetonitrile–ethyl acetate mixtures. A water content of ~5000 ppm was determined by means of a Karl Fischer titration, using a Mettler Toledo DL32 coulometer. The $^1$H-NMR spectrum of the purified compound was (500 MHz, $D_2O$, $\delta$ in ppm) 8.69 (s, 1H), 7.46 (dd, 1H, J=2.0 Hz, $J$=1.5 Hz), 7.41 (dd, 1H, $J$=2.0 Hz, $J$=1.5 Hz), 4.18 ($t$, 2H, $J$=7.5 Hz), 3.88 (s, 3H), 1.84 (q, 2H, $J$=7.5 Hz), 1.32 (m, 2H, $J$=7.5 Hz), and 0.91 ($t$, 2H, $J$=7.5 Hz). The chemical structure of BmimCl is shown in Chart 1. Although, at ambient conditions, BmimCl is solid (melting point 60 °C) (Tang et al., 2008), it may remain in a metastable supercooled liquid state for long periods of time. This supercooled BmimCl phase was used to perform the measurements.

Samples of two different radionuclides $^{18}$F and $^{14}$C were prepared. In both cases, we used glass scintillation vials of 22 ml containing pure BmimCl. For the experiments with $^{18}$F, a few droplets of physiological solution of 2-deoxi-2($^{18}$F)fluorine-D-glucose were added to approximately 12 ml of ionic liquid. For the experiments with $^{14}$C, a few droplets of a glucose water solution ($10^{-3}$% m/m of ($^{14}$C)glucose and $10^{-1}$% m/m of $CH_2O$) were added to approximately the same amount of ionic liquid. The commercial scintillation cocktail UG-AB™ was used for reference measurements.

### 2.2. Scintillation measurements

All scintillation measurements were performed at room temperature (20 ± 1 °C) using a TDCR system described in detail in a previous paper (Arenillas and Cassette, 2006). The methodology was based on counting double and triple coincidences, using the MAC3 module (Bouchard and Cassette, 2000). At these conditions, the high viscosity of the ionic liquid ( > 300 cP, (Liu et al., 2008)) hinders a rapid and effective homogenization of the samples. For this purpose, usually a heating at ~60 °C is required. Special care was taken to thermostatize the samples at room temperature after being heated, because samples improperly thermostatized could lead to spurious signals in the phototubes.

## 3. Theoretical approach on TDCR-based methods

### 3.1. TDCR method

The triple-to-double coincidence ratio (TDCR) method is based on the detection of scintillation photons using three photomultipliers in coincidence. The arrangement of detectors makes possible to obtain the experimental relationship between triple coincidences and the logical sum of double coincidences ($T/D$). If one assumes that there are no significant differences between the photomultipliers, the theoretical ratio for the counting efficiencies of the triples ($e_T$) and the logical sum of double coincidences ($e_D$) is given by (Broda et al. 2007)

$$\frac{e_T}{e_D}=\frac{\int_0^E N(E')\left(1-e^{\frac{-m(E')}{3}}\right)^3 dE'}{\int_0^E N(E')\left[3\left(1-e^{\frac{-m(E')}{3}}\right)^2-2\left(1-e^{\frac{-m(E')}{3}}\right)^3\right]dE'} \quad (1)$$

For a large number of disintegrations, the $T/D$ counting ratio converges towards the $e_T/e_D$ efficiency ratio. In the last expression, $E$ is the energy, $N(E')$ is the normalized β spectrum for the