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INVESTIGATION OF SEVERAL NEW IONIC LIQUIDS' BEHAVIOR DURING $^{210}Pb/^{210}Bi$ CHERENKOV COUNTING IN WATERS

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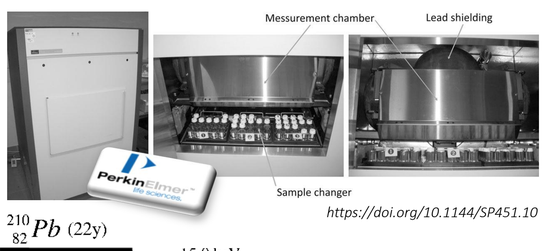
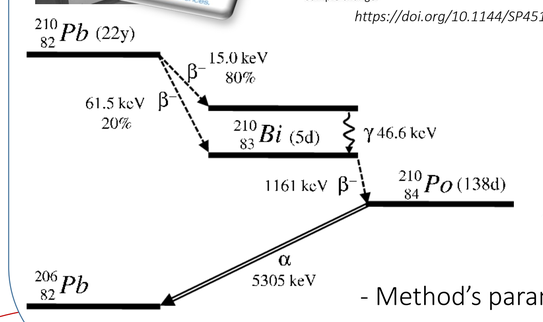
INTRODUCTION

- Determination of ^{210}Pb content in aqueous systems is carried out for radiological safety estimations and in studies of different environmental and marine processes.
- Monitoring of ^{210}Pb in water samples requires methods which are rapid, sensitive and precise since its natural levels can be very low.
- We present an investigation of a possibility to determine $^{210}Pb/^{210}Bi$ content directly without any sample pre-treatment, via Cherenkov radiation detection on a Liquid scintillation (LS) counter Quantulus 1220.
- The main aim was to investigate the performance of several newly synthesized ionic liquids (ILs) which can act as wavelength shifters, thus significantly increasing the detection efficiency of Cherenkov radiation and decreasing the detection limit during ^{210}Pb quantification.
- To better understand the mechanism of wavelength-shifting, the influence of the change of cation and anion structure for five different ILs was investigated.

METHOD'S ESSENTIALS





- Calibration vials 20 mL with different ^{210}Pb activities were prepared in three probes by adding the certified activity to distilled water after which were allowed 50 days to reach radioactive equilibrium and then measured in several cycles of 100 min
- Background samples: 20 mL of distilled water

$$\varepsilon = \frac{R_c - R_0}{A}$$

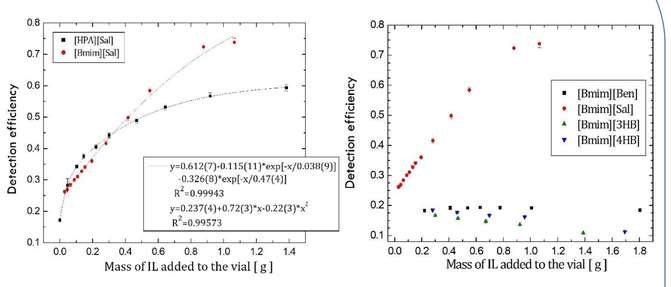
$$MDA = \frac{2.71 + 4.65\sqrt{R_0 t_0}}{V\,\varepsilon\,t_0}$$

A [Bq] - calibration sample's reference activity
ε - the detection efficiency
R_c, R_0 [s^{-1}] - the count-rates of calibration and the background sample, respectively
V[L] - the analyzed volume of a water sample
MDA [Bq L^{-1}] - Minimal Detectable Activity
t_0 [s] - the background counting time

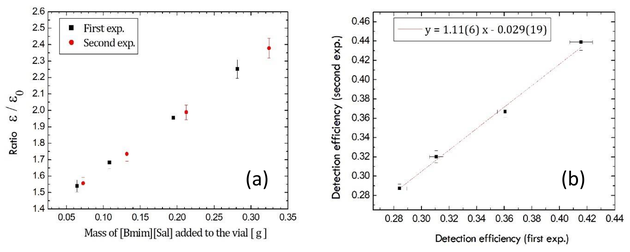
- Method's parameters without IL's addition:

$$\varepsilon = 14.44(21)\%, \qquad MDA = 0.85 \text{ Bq L}^{-1} \text{ for } t_0 = 1000 \text{ min}$$

IL's INFLUENCE ON DETECTION EFFICIENCY



- When the added IL's mass exceeds 0.5 g, [Bmim][Sal] becomes more efficient than [HPA][Sal]
- The increment in the detection efficiency from 15% to >70% in the presence of 0.9 g of [Bmim][Sal] reduces detection threshold by more than 4 times.
- The addition of ILs did not alter the shape or position of Cherenkov spectra, suggesting that ILs act as wavelength shifters.
- No other IL except [Bmim][Sal] caused the detection efficiency increment, so the cation structure does not increase the count rate.



Reproducibility tests for two independent experiments:
(a) Efficiency ratio for similar addition of [Bmim][Sal]
(b) correlation between the obtained efficiencies

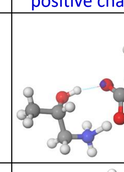
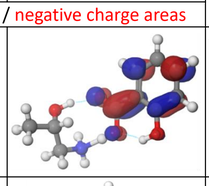
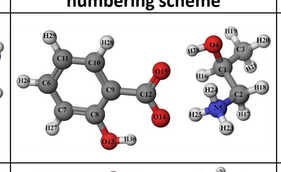
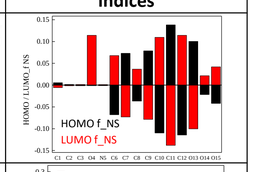
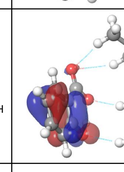
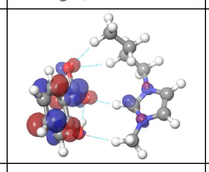
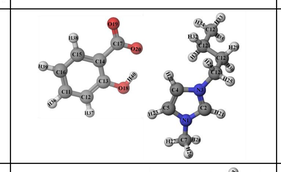
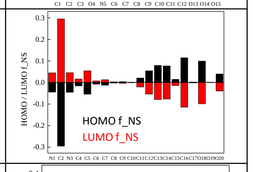
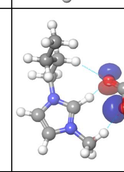
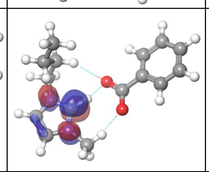
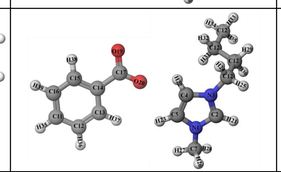
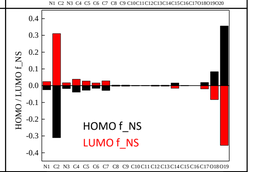
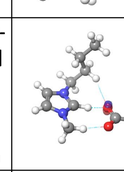
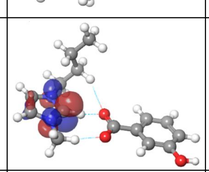
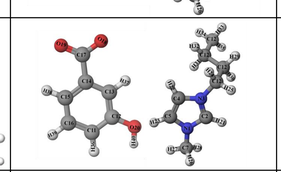
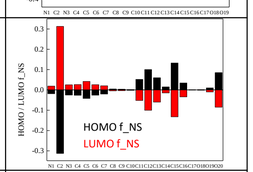
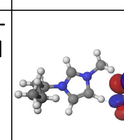
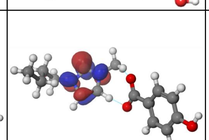
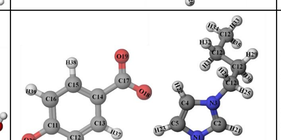
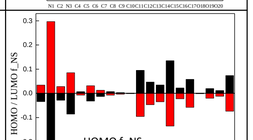
RESULTS OF MOLECULAR SIMULATIONS – A DESCRIPTION OF SCINTILLATING ACTIVITY

DFT calculations were applied using Jaguar 9.0 software (Schrödinger Materials Science Suite 2015-4). The B3LYP exchange-correlation functional with the empirical correction for dispersion (B3LYP–D3) was used with 6–31+G(d,p) basis set. Generalized Valence Bond Perfect-Pairing (GVB-PP) was used, a pseudospectral method that is extended to electron correlation methods, that can predict very accurate excitation energies, rotational barriers and bond energies. The Continuum solvation model (Generalized Born model) was applied. To ensure the validity of the obtained structures, geometrical optimizations were followed by harmonic frequency analysis.

The Fukui functions are partial derivatives of the electron and spin density concerning a change in either the electron count or the unpaired spin count, and predict the scintillating potential of the compound:

$$f^{\pm} = \frac{\rho^{N\pm\delta}(r) - \rho^{N}(r)}{\delta}$$

N - the number of the electrons in the reference state of the molecule, δ - a fraction of an electron

Ionic liquid (IL) and its chemical structure	HOMO orbitals	LUMO orbitals	ILs' structure and atom-numbering scheme	Representation of Fukui indices
	positive charge areas / negative charge areas			
2-hydroxypropylammonium salicylate [HPA][Sal]				
1-butyl-3-methylimidazolium salicylate [Bmim][Sal]				
1-butyl-3-methylimidazolium benzoate [Bmim][Ben]				
1-butyl-3-methylimidazolium 3-hydroxybenzoate [Bmim][3HB]				
1-butyl-3-methylimidazolium 4-hydroxybenzoate [Bmim][4HB]				

Compound	E_{HOMO} [eV]	E_{LUMO} [eV]	ΔE_{gap} [eV]
[HPA][Sal]	-6.002	-1.075	4.927
[Bmim][Sal]	-6.024	-0.778	5.245
[Bmim][Ben]	-5.292	-0.537	4.755
[Bmim][3HB]	-5.123	-0.520	4.603
[Bmim][4HB]	-4.791	-1.179	3.612

- Excitation potential of molecules is predicted from energy of the highest occupied molecular orbital, i.e. region of electron donors (HOMO) and the lowest unoccupied molecular orbital, i.e. region of electron acceptors (LUMO).
- ΔE_{gap}, HOMO–LUMO gap energy, indicates the electronic excitation energy, describing the scintillating potential of a substance.
- f_NS indicates the change in electron density about atom when the molecule undergoes a reaction in which its spin multiplicity changes and describes how easily a molecule can be excited.

- [HPA][Sal] has the highest and positive HOMO values. The most positive f_NS values indicate the largest changes in the electron density at HOMO orbitals in reaction with the change of the spin shape.
- By comparing ILs with the same cation and a different anion, [Bmim]+ has better properties as a cation because the whole ring has positive LUMO f_NS values.
- [Ben]- anion is inert in terms of the electron density. The most LUMO f_NS values for [Bmim][Ben] are near zero. LUMO f_NS values are concentrated around the oxygen atom of the carboxyl group (O19) with a pronounced negative value indicating its poor excitation.
- [Bmim][Sal] is the most active scintillator because all LUMO f_NS values around the cation ring are positive. ΔE_{gap} values indicate that [Bmim][Sal] demands more energy to become excited and emit a photon.

CONCLUSIONS

- The performance of several newly synthesized ionic liquids during $^{210}Pb/^{210}Bi$ Cherenkov counting on a LS counter Quantulus 1220 was investigated.
- Among few ILs with the same cation structure, [Bmim]+, only the one with salicylate as an anion increased the detection efficiency, [Bmim][Sal], with more significant impact on the efficiency in comparison with [HPA][Sal].
- The increment in detection efficiency in the presence of 0.9 g of [Bmim][Sal], reduces $^{210}Pb/^{210}Bi$ detection threshold for more than 4 times.
- ILs' behaviour could be explained via analysis of their HOMO f_NS and LUMO f_NS values. Salicylates act as wavelength shifters, consequently increasing the detection efficiency of Cherenkov counting.

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