INVESTIGATION OF THE EFFECTS OF -OH GROUP SUBSTITUTION ON THE RADIATION STABILITY OF FAP (FLUORO ALKYL PHOSPHATE) BASED IMIDAZOLIUM IONIC LIQUIDS

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Abstract

The radiation stability and the mechanism for FAP imidazolium ionic liquids (ILs) have been investigated owing to their superior hydrolytic stability and ultra hydrophobic nature. The ILs were subjected to very high radiation doses ranging from 50 kGy to 500 kGy. Various characterization studies involving density, viscosity, refractive index, conductivity, thermal stability and electrochemical window were performed on the irradiated ILs to determine the radiation effects on these properties. Qualitative studies i.e. NMR & Mass spectrometric studies were conducted on the ILs to identify the radiolytic products and the amount of decomposition was found to be <5% at higher radiation doses of 400 kGy. Introduction of -OH group in the alkyl side chain of the imidazolium moiety resulted into significant changes in the physical properties of these ILs with respect to their onset temperatures, conductivity and electrochemical window. Besides these, the H2 gas yields of the ILs were determined and found to be comparable to that of a radiolytically stable aromatic compound, benzene. Through transient spectroscopic studies, we could delineate the mechanism for the radiation induced changes in the physicochemical properties of the non-hydroxyl and hydroxyl containing FAP ILs.

Introduction

Room Temperature Ionic Liquids (RTILs) are a rapidly expanding family of condensed-phase media with important applications in synthesis, extraction, catalysis and electrochemistry [1]. In the present scenario, RTILs are being considered as potential candidates in the reprocessing of spent nuclear fuel. It is therefore imperative to study the radiation chemistry of ILs to determine their radiolytic products and degradation pathways. No surprise that several radiation stability studies on ILs have already been reported. Most of these studies have been carried out on imidazolium ILs having anions such as PF$_6^-$, BF$_4^-$ or halogens. Essentially, these ILs have been found to be hydrolytically unstable giving off highly toxic and corrosive HF. Further, the application of hydrophobic ILs in nuclear separations may put the ILs both in high radiation fields and in contact with aqueous raffinate containing 1-6 M HNO3. Amongst various ILs, imidazolium ILs with bulky FAP (tris(perfluoroalkyl) trifluorophosphate) anion are ultra hydrophobic and possess excellent hydrolytic stability. Therefore, we performed an assortment of characterization and qualitative studies to explore the radiation stabilities of FAP ILs in the radiation doses, ranging from 50 to 500 kGy. Pulse radiolysis experiments were carried out to determine the transient species and their kinetic behavior on radiolysis.
Materials and methods

1-ethyl-3-methylimidazolium tris (pentafluoroethyl) trifluorophosphate, \([\text{EMIM}]\text{[FAP]}\) and 1-(2-Hydroxyethyl)-3-methylimidazolium tris (pentafluoroethyl) trifluorophosphate, \([\text{EOHMIM}]\text{[FAP]}\) were obtained from Merck KGaA, Darmstadt, Germany, with a purity > 99%. All other chemicals were of spectroscopic grade. The ILs were irradiated with a 7 MeV electron beam (FWHM ~ 2 \(\mu\)s) obtained from a linear accelerator (LINAC, in conjugation with Pulse radiolysis system). The electron pulse used for carrying out the Pulse radiolysis experiments was 500 ns, while the dose per pulse was kept as 12 Gy. The structures of the ILs studied are shown below.

![Structures of ILs](image)

Results and discussion

On irradiation, both the ILs exhibited color evolution which further became intense with the increase in radiation dose. However, the color darkening was more in case of –OH group containing IL i.e. \([\text{EOHMIM}]\text{[FAP]}\). The color evolution in \([\text{EMIM}]\text{[FAP]}\) at various radiation doses has been shown in the inset of Fig.1. This gives the indication of the radiolytic degradation occurring in the ILs. A typical optical absorption spectra of irradiated and unirradiated \([\text{EMIM}]\text{[FAP]}\) are shown in Fig.1. It was observed that \([\text{EMIM}]\text{[FAP]}\) displayed linear variation in the absorbance values (at 290 nm) with the radiation dose, while such trend was not observed in the case of \([\text{EOHMIM}]\text{[FAP]}\). This result indicates, the -OH group can influence the radiolytic degradation pathways of \([\text{EOHMIM}]\text{[FAP]}\).

Qualitative studies such as NMR and Mass spectrometry were conducted on the pre- and post-irradiated ILs to identify the radiolytic products and the amount of degradation. Predominantly, the oligomeric species of imidazole and its derivatives were observed however, their amounts were found to be very less (<0.5%) [2]. Nevertheless, the oligomeric products of imidazole are chromophoric in nature having high molar extinction co-efficient (\(\epsilon\)) of the orders of 10^4 \(\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}\) and exhibit similar optical absorption spectral features as in the present case of irradiated ILs. Therefore, the color evolution and the appearance of absorption peaks in case of irradiated ILs can be ascribed to \(\pi-\pi^*\) transition that originates from the radiolytic products derived from the imidazolium cation.

![Absorption Spectra](image)

Fig.1: UV-VIS absorption spectra of pre-anti post-irradiated \([\text{EMIM}]\text{[FAP]}\). Inset: Picture showing the color variation of IL on irradiation.

Various characterization studies were performed on the irradiated ILs to determine the radiation effects on their properties i.e. colour, density, viscosity, refractive index, conductivity, thermal stability and electrochemical window. As can be noticed from Table 1, the variation in the values of aforementioned properties of \([\text{EMIM}]\text{[FAP]}\) was very less even a high radiation doses of 400 kGy. While, significant decrease in the thermal stability and the conductivity values was observed for –OH group containing IL on irradiation. Besides, the gaseous products evolution is a crucial factor to be considered for any industrial or reactor scale application. Therefore, \(\text{H}_2\) gas yields (G (H2)) were measured from the irradiated FAP ILs ((7.6 \pm 0.2) \times 10^{-9} \text{ mol/J} for \([\text{EMIM}]\text{[FAP]}\) and (8.5 \pm 0.4) \times 10^{-9} \text{ mol/J} for \([\text{EOHMIM}]\text{[FAP]}\)) and were found to be...
almost equivalent to that of radiolytically stable aromatic compounds, i.e. benzene ((6.5 ± 0.4) x 10^-9 mol/J) [2].

Transient spectroscopic studies were carried out by Pulse radiolysis technique to delineate the mechanism for the radiation induced changes in the physicochemical properties of the non-hydroxyl and hydroxyl containing FAP ILs. Both the ILs give rise to similar transients with absorption peaks at 320 nm and a weak shoulder at 370 nm (Fig. 2A&B). However, the absorbance at 320 nm in case of [EOHMIM][FAP] is 1.3 times higher than that in case of [EMIM][FAP]. A faster rate of formation of the transients was observed in case of [EOHMIM][FAP] (5.7 x 10^6 s^-1) cf. [EMIM][FAP] (3.26 x 10^6 s^-1). Furthermore, a marked difference was noted in the transient decay behavior of both the ILs in the presence of O_2. As can be observed from Fig. 2C, the formation of a new species was evident in case of [EOHMIM][FAP] and was quite prominent while measuring at 370 nm. It was inferred that the formation of alkyl radical at the ethoxy side chain of the cation is quite likely as the addition of O_2 to this radical would form a peroxyl radical which shows a strong absorption in the wavelength region 320-370 nm [2]. Thus, it becomes clear that the two ILs behave differently in radiation environment which has also been reflected in the number and yield of products.

Conclusions

All the results discussed here clearly indicate the hidden potential of the FAP imidazolium ILs to be a good solvent for various applications involving high radiation fields. Also, we have clearly demonstrated that a simple functionalization of the molecular structure of these ILs might cause marked differences in the reactivity, reaction center and the nature of the radiolytic products, which eventually lead to the significant changes in their physicochemical properties.

References