

## **Hydrolysis of Tetrafluoroborate and Hexafluorophosphate as Counter Anions in Imidazolium-Based Ionic Liquids**

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In recent years, ionic liquids (ILs) have gathered special attention from the scientific community and an exponential increase of studies involving different features, properties and applications of ILs have been presented hitherto in the literature. Their particular physicochemical characteristics such as high solvation ability and coordination properties, general non-flammability, wide liquidus range, wide electrochemical window, high thermal stability and negligible vapor pressures make them an environmentally friendly alternative for the ordinary volatile organic solvents (VOC), due to the reduction of the VOC emissions into the atmosphere. Nevertheless, the IL classification as green solvents should also take into account their entire life-cycle, in particular their environmental fate, possible hazardous properties, potential toxicity issues, thermal and chemical stability, and not only their effect on atmospheric emissions.

Therefore, in this work, the thermal and chemical stability of hexafluorophosphate and tetrafluoroborate-based ILs in aqueous solutions were evaluated. The experimental conditions employed allowed the study of the possible decomposition of both anions, under the influence of the pH of the aqueous solutions, as well as the temperature, and the effect of the imidazolium cation side alkyl chain length on that decomposition. Three experimental techniques were employed to fully characterize those anions' stability: electrospray mass spectrometry, nuclear magnetic resonance spectroscopy and pH measurements of the equilibrium aqueous solutions. The results noticeably indicate that it is safe to use aqueous solutions of hexafluorophosphate-based ILs at moderate temperatures while acidic conditions promote anion hydrolysis even at low temperatures. On the other hand, the tetrafluoroborate-based ILs are not water-stable compounds, since they hydrolyse under all the conditions tested and the hydrolysis extent is markedly dependent on the temperature.