Ionic liquids (ILs) are a new generation of solvents for catalysis, liquid-liquid extractions and synthesis which have been demonstrated as potential successful replacements for conventional media in chemical processes. The important properties of ILs are their high heat capacity, extremely low volatility, nonflammability, high thermal stability, wide temperature range for liquid and especially their properties fine-tuning by the right choice of the cation and/or the anion.

For ionic liquids (ILs) to be used effectively as solvents in liquid-liquid extraction, it is important to know the mutual solubilities between ILs and a second liquid phase. In this work, we address the mutual solubilities between water and ILs.

There are several based imidazolium, pyridinium, ammonium and phosphonium cation ionic liquids commercially available. Phosphonium salts are much more stable than the corresponding ammonium salts and even the imidazolium salts, which is very important for processes operating at temperatures higher than 100ºC. In addition of being slightly less thermally stable, the imidazolium cation contains protons which are not entirely inert. Finally, the fact that phosphonium salts are, in general, less dense than water, can be beneficial in product extraction by decanting aqueous systems.

The solubility of an IL in water is easily determined by optical absorption if the IL has a characteristic peak and significant absorbance at that peak (pyridinium and imidazolium salts). If the IL is aliphatic and thus has no peak in the UV region, another method to determine their solubilities in water is in need. In this work Electrospray Ionization Mass Spectrometry is proposed to experimentally determine phosphonium based ILs in water solubilities. This study focuses on hydrophobic phosphonium based ILs presenting low water solubilities. The influence of the anion substitution on the solubility was studied. The IL content in the water-rich phase was analyzed using Mass Spectrometry in the temperature range between 288 and 318 K and at atmospheric pressure. This method was validated with some hydrophobic imidazolium based ionic liquids in water. A comparison between both methods providing quantitative data was obtained. The water content in the IL-rich phase was analyzed by Karl Fischer titration.