

Ionic Liquids' Cation and Anion Influence on Aromatic Amine Solubility

Ana R. C. Morais,[†] Andre M. da Costa Lopes,[†] Ewa Bogel-Łukasik,[‡] and Rafał Bogel-Łukasik^{*,†}

[†]Laboratório Nacional de Energia e Geologia, I.P., Unit of Bioenergy, Estrada do Paço do Lumiar 22, 1649-038, Lisboa, Portugal

[‡]REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal

ABSTRACT: The mutual solubility of aniline and a series of imidazolium based ionic liquids with bis(trifluoromethylsulfonyl)-amide, chloride, dicyanamide, tetrafluoroborate, and hexafluorophosphate anions were studied. The produced results show the potential in the new solvent systems which can be used in amine chemistry. The liquid–liquid equilibrium (LLE) and solid–liquid equilibrium (SLE) measurements were performed using a dynamic (synthetic) method. The mutual solubility of aniline in bis(trifluoromethylsulfonyl)amide and hexafluorophosphate ionic liquids was complete in the examined range of temperatures. The solubility of remaining studied ionic liquids decreases with the decrease of Kamlet–Taft basicity of ionic liquid anion. In other words, the solubility was the lowest for a chloride ionic liquid and increases for dicyanamide and for tetrafluoroborate ionic liquids. Additionally, the increase of the alkyl chain length of the IL cation effects negatively the solubility of aniline in the investigated ionic liquids.

1. INTRODUCTION

Ionic liquids are chemicals that are broadly used in wide range of applications.^{1–3} Ionic liquids, together with other alternative solvents such as water and CO₂,⁴ have proven their sustainable applications in catalysis,² reactions,⁵ and separations.⁶ The continuous discovery of new ionic liquids makes them an interesting group of solvents for many applications^{7,8} especially due to their interesting solvent power^{9,10} and easily and widely tunable physicochemical properties.¹¹ Other important issue is the toxicity and biodegradability of ionic liquids.^{12,13} An often claimed disadvantage of ionic liquids is also their prices. However, the most recent achievements demonstrate that ionic liquid price can be as low as the price of classical solvents¹⁴ and still the possibility of reuse of ILs make them an excellent alternative for classical organic solvents.¹⁵ Therefore, ionic liquids as designer solvents having excellent properties and low price are an excellent medium for any reaction. Nevertheless, before any chemicals including ionic liquids can be used in the reactions their potential as solvent must be scrutinized. Thus, simple although very useful study permits the examination of the solubility of chemical compounds in ionic liquids. In particular, the knowledge about interactions existing between ionic liquids and other chemicals is exceptionally important, as it allows designing greener and more sustainable chemical processes.

One of the simplest primary aromatic amines is aniline. It is constituted by a phenyl ring and an amino group. Aniline, due to a high reactivity of the amine group present in the chemical structure, is broadly used in synthesis of various industrial products. The major application of aniline is directed to production of methylene diphenylene isocyanate which is commonly used to form polyurethanes, rubber processing chemicals, dyes and pigments, pharmaceuticals, and so on.¹⁶ Aniline is one of the chemicals produced worldwide on the

scale of megatons, and aniline consumption by 2015 is foreseen to reach 6.2 Mtons.¹⁷

This work is focused on mapping the solubility of aniline in several imidazolium based ionic liquids. The major aim of this work is to study the interactions that govern the solubility of aniline in a series of imidazolium ionic liquids. To the best of our knowledge, until now there are very scarce studies about the solubility of aniline in ionic liquids. Santos et al. examined the solubility of aniline in five bis(trifluoromethylsulfonyl)-amide based and five trifluoromethanesulfonate based ionic liquids. They discovered that aniline as a weak hydrophobic base is completely soluble in the [NTf₂] ionic liquids. Contrary to this discovery, hydrophilic [OTf] ionic liquids are rather poor solvents for aniline and solubility is strongly reliant on the alkyl chain length in the IL cation. The miscibility gap of systems containing aniline and trifluoromethanesulfonate shrinks with the decrease of the alkyl chain length of the cation.¹⁸ Other work shows that for the (ionic liquids + aromatic compounds) solutions the mutual solubility increases as the cation alkyl chain becomes longer and, compared to the [OTf], the [NTf₂] anion guarantees much better mutual solubility of the studied ionic liquids and the aromatic compounds.¹⁹ These contradictory results especially on the influence of alkyl chain length of ionic liquid cation guided the study presented in this work. In particular, the following ionic liquids were used: 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide [C₄mim][NTf₂], 1-butyl-3-methylimidazolium hexafluorophosphate [C₄mim][PF₆], 1-butyl-3-methylimidazolium tetrafluoroborate [C₄mim][BF₄], 1-butyl-3-methylimidazolium dicyanamide [C₄mim][N(CN)₂],

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