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A rational synthetic approach for producing quaternary ammonium halides and physical properties of the room temperature ionic liquids obtained by this way

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ABSTRACT

In the present paper the rational strategy for the high-yield solvent free synthesis of alkylammonium halides which consists in the nucleophilic addition of alkylaminoethanols to 2-chloroethanol was described. The proposed strategy was used to synthesize hydroxyl-functionalized solid ionic compounds such as dimethyl (or methyl) di-(tri)(2-hydroxyethyl) ammonium chloride and tetra-(2-hydroxyethyl) ammonium chloride, as well as novel room temperature ionic liquids (RTILs) such as dimethyl (IL-4) and methyl mono-(di-)(2-hydroxyethyl) (2-hydroxyethoxy)ethyl chloride (IL-5) all of which were characterized by FT-IR, ^{1}H and ^{13}C NMR. For the newly obtained RTILs, density (ρ) and viscosity (η) were obtained at temperatures from T = (283.15 to 353.15) K while the refractive index (n_D) was measured from T = (283.15 to 343.15) K. The data on ρ and n_D were used for calculation of the RTILs' fractional free volumes (FFV), molar refraction, and pseudo-activation energy of viscous flow. In addition, NH_3 absorption capacity of the obtained ILs was estimated gravimetrically. It was shown that this property correlates with the IL's FFV and increases by two times for IL-5 which exhibits an additional hydroxyl group compared to IL-4.

1. Introduction

Over the past decades ionic liquids (ILs) have been at the forefront of research in various fields due to a unique combination of properties which include low vapor pressure, low volatility, very low flammability and high stability, ie. characteristics typical for the so-called "green" solvents. Since their introduction in 1914 [1], ILs have become the media of ever-growing interest as promising candidates to replace the organic volatile solvents and/or catalysts in many physical and chemical processes [2]. Indeed, ILs have been already proposed as an alternative for the processes of extraction [3], chemical transformations [4], catalysis [5–9], gas separation [10–13], CO_2 sorption and capture [14–17], and many other applications [3,8,18–22]. In addition, due to the almost unlimited combinations of organic cations (derivatives of imidazolium, pyridinium, ammonium, phosphonium, etc.) and organic or inorganic anions (acetate, sulfate, halide, etc.) [23] that they can be composed of, ILs can be directionally designed to optimize a specific reaction by holding defined properties, for example, to reach a maximum yield and purity of an isolated product [2] or solubilize a long range of bio-polymers [24].

Generally, ILs are organic salts melting below 100 °C and with those being liquid roughly around 298 K are usually called room temperature ionic liquids (RTILs). With a melting point of 285 K a quaternary ammonium salt ethylammonium nitrate is apparently the first representative of the RTIL sub-class. Since then, hundreds of new ILs have been synthesized and characterized including, among many others, quaternary ammonium salts [25–27] exhibiting melting points below 100 °C.

Although the range of ILs is very wide, a basic method consisting of a single step reaction between a Lewis base and different halides is usually employed for their synthesis [19]. Since a halide

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