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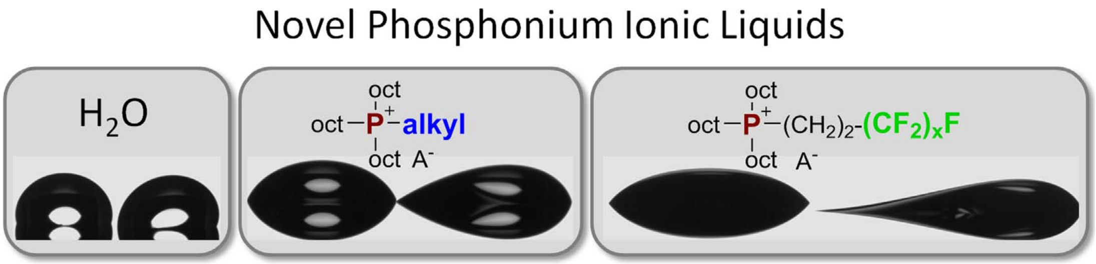
Trioctylphosphonium room temperature ionic liquids with perfluorinated groups – Physical properties and surface behavior in comparison with the nonfluorinated analogues

Daniel Rauber[a,b,*], Florian Heib[a], Michael Schmitt[a], Rolf Hempelmann[a,b,c]

[a] Institute of Physical Chemistry, Saarland University, Campus B 2 2, 66123 Saarbrücken, Germany
[b] Transfercenter Sustainable Electrochemistry, Saarland University, Am Markt, Zeile 3, 66125 Dudweiler, Germany
[c] Korea Institute of Science and Technology Europe, Campus E 7 1, 66123 Saarbrücken, Germany

GRAPHICAL ABSTRACT



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ABSTRACT

A series of novel ionic liquids (ILs) based on trioctylphosphonium-cations with attached perfluorinated chains and the anions bis(trifluoromethanesulfonyl)imide (NTf_2^-), dicyanamide ($N(CN)_2^-$) and tricyanomethanide ($C(CN)_3^-$) was synthesized. Their important physicochemical properties such as thermal behavior, solvatochromic polarities and viscosities were measured and compared to the alkyl analogues in order to investigate the influence of fluorination. The characteristic wetting behavior of these ILs on a hydrophobic modified surface was analyzed using the *high-precision drop shape analysis* (HPDSA) approach as this method is suitable to analyze highly non-symmetrical droplets. For the fluorinated ILs a more pronounced effect on the thermal transitions with increasing side chain length was found. The introduction of fluorinated alkyl groups leads to anion dependent decomposition temperatures, higher overall viscosities and a non-Newtonian flow shear thinning at higher shear rates. Furthermore, the fluorinated ILs showed a modified wetting behavior on the investigated surface, which was found to result in lower contact angle values and higher pinning compared to the non-fluorinated ILs.

1. Introduction

Ionic liquids (ILs) are a class of highly diverse functional solvents of organic salts with melting points below 100 °C and an unique property combination [1]. The subclass of room-temperature ionic liquids (RTILs) having melting points below ambient temperature is of special concern for most practical applications. ILs have a negligible vapor pressure along with inflammability, intrinsic conductivity, high electrochemical and thermal stability as well as wide liquid ranges and in general a good ability to solve both organic and inorganic compounds

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[*] Corresponding author at: Institute of Physical Chemistry, Saarland University, Campus B 2 2, 66123 Saarbrücken, Germany.
E-mail address: daniel.rauber@uni-saarland.de (D. Rauber).

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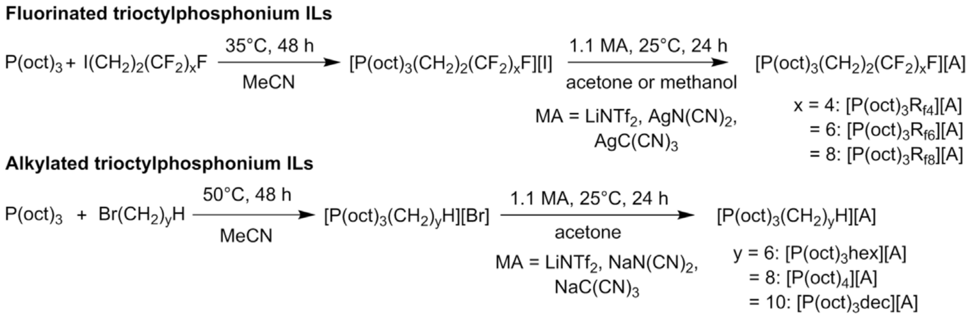

Scheme 1. Synthesis of the fluorinated and alkylated trioctylphosphonium-based ILs.

[2]. The properties of these "designer solvents" or "functional solvents" [3] are tailorable in a very wide range by their chemical composition and can be tuned depending on the demands of special processes, applications, solvent-systems etc. [4,5]. They have attracted a remarkable increase in interest throughout many scientific disciplines such as chemistry, physics, engineering and material science in the last decades as they offer completely novel opportunities for synthesis [6], analysis [7] or process technologies [8] along with the potential to optimize and improve existing technologies [9,10]. The properties of ILs can be fine-tuned by the nature of the anion and cation as well as through the introduction of additional functional groups. The incorporation of functionalities expands the possibilities of the "task-specific ILs" giving them additional desirable properties which are not achievable solely by cation-anion combinations. One functional segment of interest for ILs are perfluoroalkyl-segments as the resulting fluorous or fluorinated ILs (FILs) [11] show an altered behavior which is easily adjustable by common synthetic methods. The usage of FILs includes for example solvents for multiphasic systems [12], catalysis [13,14], as surfactants [15–17], media for CO_2-absorption [18,19], gas separation [20] or tribological applications [21,22]. As there is an immense number of possible ILs [23] it is highly important to know about the trends and properties of ILs for basic research and practical applications. Of special concern are the surface properties and adhesion of ILs as most of their applications include some kind of solid-liquid interfaces [24]. In addition the determination of the ionic liquid wetting behavior gives insight into structural organization of these solvents near solid surfaces [25] and their suitability as probe fluids [26]. As the IL surface behavior [27], such wetting and dewetting processes, is of high industrial relevance, it was subject to several studies [28–30] which are almost completely limited to imidazolium based ILs [31]. The investigation of ILs based on other cations such as the phosphonium is desirable since these solvents exhibit often superior properties such as higher degree of lipophilicity and improved electrochemical, thermal and chemical stability making them a better choice for selected applications [32]. In this study we prepared a series of novel FILs based on the trioctylphosphonium cation with perfluoroalkyl-groups of different chain lengths with either bis(trifluoromethanesulfonyl)imide (NTf_2^-), dicyanamide ($N(CN)_2^-$) or tricyanomethanide ($C(CN)_3^-$) anions to investigate the modification of the properties by the introduction of this functional groups. The substituted trioctylphosphonium cations were chosen as the long alkylchains are known to lead to comparably low viscosities despidte their large molecular size, high degree of lipophilicity as well as low glass transition and melting temperatures. This property combination is often desirable for technical applications since it allows fast thermal and mass transport, the absence of water for systems sensitive to hydrolysis and high operation temperature intervals as well as easy handling of RTILs. The physicochemical properties and wetting behavior of the novel FILs were compared to the corresponding non-fluorinated tetraalkyl IL analogues (AILs) to directly show the effect of fluorination on the properties of this substance class. Due to the comparably size of the attached fluorocarbon segment to the three octyl chains at the phosphonium core of the cation the influence of fluorination on the wetting behavior in the investigated ILs is demonstrated directly.

2. Experimental

2.1. Materials

Full details about the used reagents and their suppliers along with the synthesis protocols and characterization methods for the prepared ILs are given in the supporting information.

2.2. Syntheses of the perfluorinated and alkylated trioctylphosphonium ILs

The fluorinated and nonfluorinated phosphonium ILs were synthesized by nucleophilic substitution of the 1*H*,1*H*,2*H*,2*H*-perfluoralkyl iodides or 1-bromoalkanes with trioctylphosphine. The resulting quaternary phosphonium halide salts were then transferred to the [NTf_2], [$N(CN)_2$] or [$C(CN)_3$] ILs by means of metathesis reactions with the lithium, sodium or silver salts (MA; M = metal-cation; A = anion) depending on the type of exchanged halide. The preparation of the investigated ILs is sketched in Scheme 1. Prior to all experiments the samples were dried in oil-pump vacuum at 50 °C for two days under intensive stirring. Karl-Fischer-titration showed water-contents for the dried ILs were below 200 ppm.

2.3. Thermal properties

Glass-, phase-transition- and melting points were measured by means of differential scanning calorimetry (DSC) on a DSC 1 STARe System (Mettler Toledo, Gießen, Germany) equipped with a liquid nitrogen cooling system. Vacuum dried samples of about 15 mg were sealed in aluminum crucibles and heated with a rate of 10 °C/min to 100 °C and kept at this temperature for 10 min to remove thermal history. In the next dynamical step the samples were cooled with a cooling rate of −1 °C/min to −120 °C followed by a 10 min isothermal treatment. The samples were subsequently heated with +1 °C/min to 100 °C. All experiments were repeated with three different samples of each ILs to ensure the correct determination of glass-, phase- and melting temperatures. Decomposition temperatures were determined by means of thermogravimetric analysis on a TG F1 Iris (Netzsch, Selb, Germany) using weighted samples of approximately 10 mg. The samples were heated applying a nitrogen flow of 25 mL/min and a heating rate of 10 °C/min from 30 °C to 550 °C. Decomposition temperatures are given as extrapolated onset temperatures.

2.4. Polarity measurements

Relative molecular polarities were measured using the two solvatochromic dyes Reichardt's betaine Dye and Nile Red dissolved in the bulk ionic liquids. The determination of the UV/Vis spectra was carried out on an UV Specord (Analytic Jena, Jena, Germany) in a thermostated measuring cell at 25 °C. For the sample preparation a solution of either