



The effect of position and length of alkyl substituents in pyridinium based ionic liquids on temperature dependent transport properties

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ABSTRACT

The effect of position and length of alkyl substituent in pyridinium based ionic liquids (IL) has been studied at various temperatures. The IL investigated contained the bis(trifluoromethanesulfonyl)imide (NTf₂) anion combined with 1-alkyl-3,5-dimethylpyridinium or 1-alkyl-2,3-dimethylpyridinium cations, respectively. Data for the conductivity 0–80   C, the viscosity 10–70   C, density 0–80   C and thermal expansion coefficients 0–80   C of the ionic liquids [B23MMPYR][NTf₂], [B35MMPYR][NTf₂], [O23MMPYR][NTf₂], [O35MMPYR][NTf₂] are reported. The viscosity and conductivity data obtained could be well described with the empirical Vogel–Fulcher–Tammann equation. Based on the molar conductivities and viscosities measured from 10 to 70   C, a significant influence of the position of the methyl substituents in the cation on the transport properties has been found. Walden plots of these data demonstrate that the investigated compound can be classified as high ionicity ionic liquids. IL containing 1-alkyl-2,3-dimethylpyridinium cations were found to be closer to the “ideal” KCl line suggesting less ion association compared to their 1-butyl-3,5-dimethylpyridinium homologues.

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1. Introduction

There is a still growing interest in ionic liquids (IL) in general and room temperature ionic liquids (RTIL) in particular resulting from their fascinating and outstanding properties and wide range of potential applications. Typically, IL contain bulky organic cations with a low degree of symmetry and/or delocalized charge. Prominent examples are based on imidazolium, pyridinium, pyrrolidinium or phosphonium cations combined with anions such as tetrafluoroborate (BF₄[−]), hexafluorophosphate (PF₆[−]) and bis(trifluoromethylsulfonyl)imide (NTf₂[−]) [1–3]. By changing the combination of ions, physicochemical properties such as polarity, viscosity, solvation ability, melting point, thermal and electrochemical stabilities can be modified [4–7]. Consequently, IL have been extensively studied and applied in diversified fields of research, beside applications in industrial processes [8–12]. However, these require knowledge about their physicochemical properties such as densities, conductivities, viscosities and thermal expansion coefficients to optimize large-scale processes involving ionic liquids. In extraction processes, for instance, many studies

are still undergone to better understand the influence of the cation and anion pairs on the extraction ability and selectivity of these compounds toward pollutants. Ionic liquids are also very promising in electrochemical applications. Since they are liquids at low temperatures, exhibit high thermal decomposition temperatures, wide electrochemical windows and high ionic conductivity, they can be used as ionic conductors in electrochemical applications such as solar cells, batteries or electrodeposition processes [9].

Most ionic liquids studied recently are based on cyclic quaternary ammonium, among which the imidazolium is by far the most extensively studied cation [1,4,8]. Fewer deal with quaternary phosphonium or ternary sulfonium cations [3,13]. A few works report the physico-chemical properties of ionic liquids based on pyridine or methylpyridine [14–16]. Recently, the Walden plots of ionic liquids containing methylpyridinium cations have been reported [16]. Ionic liquids based on methyl substituted cations appeared to be good ionic conductors behaving as nearly ideal electrolytes. Nevertheless, the electrochemical stability of such compounds was reported to be rather low due to a high reduction potential as compared to ionic liquids containing imidazolium or saturated pyrrolidinium or piperidinium cations.

Much fewer reports deal with ionic liquids containing dimethylpyridinium or trimethylpyridinium cation rings [14,17]. Notwithstanding, these substances turned out to be especially promising for a variety of applications. For example, IL based on dimethylpyridinium cations have recently been successfully

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applied in deep oil desulfurization processes [18]. Furthermore, recent investigations revealed that these compounds exhibit lower solubilities in water and lower water contents, respectively compared to other ionic liquids based on pyridinium or imidazolium cations [17]. Information about transport properties of dimethyl- and trimethylpyridinium based IL is still scarce.

In order to provide a better understanding of the effect of position, length and number of alkyl substituents on the physicochemical properties of pyridinium-based IL, we studied four compounds exhibiting closely related cations, namely 1-alkyl-2,3-dimethylpyridinium and 1-alkyl-3,5-dimethylpyridinium and [NTf₂] as anion. In the present study, we report densities, viscosities, conductivities and thermal expansion coefficients of 1-butyl-2,3-dimethylpyridinium bis(trifluoromethylsulfonyl)imide [B3M5MPYR][NTf₂], 1-octyl-2,3-dimethylpyridinium bis(trifluoromethylsulfonyl)imide [O2M3MPYR][NTf₂], 1-butyl-3,5-dimethylpyridinium bis(trifluoromethylsulfonyl)imide [B3M5MPYR][NTf₂] and 1-octyl-3,5-dimethylpyridinium bis(trifluoromethylsulfonyl)imide [O3M5MPYR][NTf₂] at various temperatures. Consistent with previous studies, viscosity and conductivity data could be well fitted with the Vogel–Fulcher–Tammann (VFT) equation. Data have further been compared to other pyridinium homologues.

In addition, in order to study the difference in Walden plots, and the degree of association for IL of similar sizes, such as [B2M3MPYR][NTf₂] and [B3M5MPYR][NTf₂], or [O2M3MPYR][NTf₂] and [O3M5MPYR][NTf₂], density, viscosity and conductivity measurements have also been used to fit fractional forms of the Walden relationship.

2. Experimental

2.1. Synthesis

Synthesis of all ionic liquids studied here have been reported previously [17]. Briefly, ionic liquids were synthesized in two steps. First, 1-bromobutane or 1-bromooctane was mixed with 2,3-dimethylpyridine or 3,5-dimethylpyridine in a round-bottom flask containing acetonitrile. The solution was then stirred under reflux for 24 h. The solvent was then removed by rotary evaporation. The white powder, corresponding to a bromide ionic liquid, was washed with cyclohexane, diethyl ether and ethyl acetate and dried under vacuum for at least 12 h.

Corresponding ionic liquids containing [NTf₂] anion were then obtained by metathesis, mixing bromide IL with lithium bis(trifluoromethanesulfonyl)imide in a minimum amount of water and stirred for 12 h. The resulting lower phase was then extracted with dichloromethane, and further washed by dichloromethane/water extraction. The resulting clear light yellowish IL was then set up under vacuum for at least 12 h. Due to the high solubility of lithium salts in water (LiBr and LiNTf₂), several washings of the IL with water and dichloromethane mixtures was carried out to remove lithium impurities in the IL.

Purity was checked by ¹H and ¹³C NMR. See reference for details [17]. Bromide impurities were checked with silver nitrate test and found to be below 100 ppm. ESI-MS was carried out for all samples studied here with a Equire 3000 Plus spectrometer from Brücker Daltonics. Results are as following:

[B2M3MPYR][NTf₂]: (*m/z*): calc. for C₁₁H₁₈N (M⁺): 164.267; found: 164.150; calc. for C₂S₂O₄NF₆ (M⁻): 280.146; found: 279.850.

[O2M3MPYR][NTf₂]: (*m/z*): calc. for C₁₁H₁₈N (M⁺): 220.374; found: 220.240; calc. for C₂S₂O₄NF₆ (M⁻): 280.146; found: 279.860.

[B3M5MPYR][NTf₂]: (*m/z*): calc. for C₁₁H₁₈N (M⁺): 164.267; found: 164.160; calc. for C₂S₂O₄NF₆ (M⁻): 280.146; found: 279.850.

[O3M5MPYR][NTf₂]: (*m/z*): calc. for C₁₁H₁₈N (M⁺): 220.374; found: 220.220; calc. for C₂S₂O₄NF₆ (M⁻): 280.146; found: 279.840.

The presence of impurities was not detectable and the signal over noise ratio was always above 1000 for all the samples studied. Under fragmentation conditions of the cation the formation of dimethylpyridine fragment was observed.

2.2. Water content

The water content of each IL was determined by coulometric Karl–Fischer titration, using an Abimed MCI analyser (Model CA-02). Water contents for the four IL were 422 ppm for [B2M3MPYR][NTf₂], 312 ppm for [O2M3MPYR][NTf₂], 227 ppm for [B3M5MPYR][NTf₂] and 151 ppm for [O3M5MPYR][NTf₂].

2.3. Conductivity

Conductivity measurements have been performed at ambient temperature (25 °C) and within a temperature range between 0 and 80 °C in intervals of 10 °C. Measurements were carried out with an in-house built apparatus described by Barthel and coworkers equipped with a precision thermostat, symmetrical Wheatstone bridge with Wagner earth, sine generator and resistance decade [19,20]. The thermostat was stable to <0.003 °C over the investigated temperature range. A set of three three-electrode capillary cells with cell constants ranging from 54 m⁻¹ to 470 m⁻¹ was used. Cell constants were determined with aqueous KCl solutions according to a procedure described by Barthel et al. [21] To eliminate electrode polarization effects, resistances *R* were measured at frequencies *ν* between 480 Hz and 10 kHz, and extrapolated to $R_{\infty} = \lim_{\nu \rightarrow \infty} R(\nu)$ to yield $\kappa = C/R_{\infty}$ [20]. The relative uncertainty of the electrical conductivities was estimated to be less than 0.5%.

The temperature dependence of cell constants was first described by Robinson and Stokes [22] and experimentally verified by Barthel and coworkers [19,21]. As the application of the temperature coefficient, β , changed the electrical conductivities only within the given uncertainty limits, the temperature dependence of the cell constants could be neglected for the present measurements.

2.4. Viscosity

Viscosity measurements were carried out on a Bohlin rheometer (type CVO 120 High Resolution) under argon atmosphere at controlled temperature. The temperature calibration was performed with a standard viscosity oil and a platinum resistance thermometer within a temperature range between 10 and 70 °C. The accuracy in temperature was estimated to be better than ±0.2 °C. Samples were studied at shear rates ranging from 0.25 to 500 s⁻¹. For all neat IL a Newtonian behavior was observed within the measured temperature range. The relative uncertainty of the dynamic viscosities was estimated to be less than 5%.

2.5. Density

Density measurements were carried out on a vibrating tube densimeter (DSA5000 AntonPaar) under argon atmosphere at controlled temperature. The precision on the density is around 0.000005 g/cm³.

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