



Measurements of the density, refractive index, electrical conductivity, thermal conductivity and dynamic viscosity for tributylmethylphosphonium and methylsulfate based ionic liquids



Eva Rodil^{a,*}, Alberto Arce Jr.^b, Alberto Arce^a, Ana Soto^a

^a Department of Chemical Engineering, Universidade de Santiago de Compostela, 15782 Santiago de Compostela, Spain

^b School of Engineering, Universidade de A Coruña, 15403 Ferrol, Spain

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ABSTRACT

In this work, the effect of ion and temperature change on the thermophysical properties of several ionic liquids was investigated. Five room-temperature ionic-liquids were selected: tributylmethylphosphonium chloride ([P₄₄₄₁]Cl), tributylmethylphosphonium bis(trifluoromethylsulfonyl) amide ([P₄₄₄₁][NTf₂]), tributylmethylphosphonium methylsulfate ([P₄₄₄₁][MeSO₄]), 1-methylpyridinium methylsulfate ([C₁py][MeSO₄]), and 1-butyl-3-methylimidazolium methylsulfate ([C₄mim][MeSO₄]). Densities, refractive indices, electrical conductivities, thermal conductivities and dynamic viscosities were reported ranging from (283.15 to 343.15) K at atmospheric pressure. The thermal stability of all the ionic liquids has been also studied at a heating rate of 5 K min⁻¹ using a thermogravimetric analyzer. The effect of temperature change on density was discussed in terms of ion volume, and the influence on electrical conductivity and dynamic viscosity was discussed in terms of ion mobility. The effect of the variation of the ion was discussed in terms of size, steric effects and interaction strength between cation and anion. Finally, the temperature dependence for density, refractive index and thermal conductivity was correlated with linear functions, while a Vogel-Fulcher-Tammann type function was used for the correlation of the temperature dependence for electrical conductivity and dynamic viscosity.

1. Introduction

A large number of researchers are devoted to demonstrating the great potential that ionic liquids (ILs) have for practical applications due to their nature and qualities [1]. Among these applications, their use as heat-transfer fluids can be highlighted [2]. Recent works [3–9] show that the behavior of the thermal properties with temperature of ILs is similar to those of molecular liquids, including commercial heat-transfer fluids, such as the Dowtherm A[®] [10]. For this reason, the knowledge of ILs temperature dependence properties is of major importance for their application in practical processes. Such information, considering the diverse nature and large number of ILs, raises the development of reliable predictive models for which accurate experimental determinations are critical.

In the current bibliography, a significant number of studies of ionic-liquid families can be found. Careful selection and study of complete sets of compounds, representing different families, can provide information about the relationships between the property and the IL structure and allow to obtain suitable correlations, state equations, or other models for these properties. For example, Bhattacharjee et al.

[11], Deive et al. [12] and Adomavá et al. [13] study the thermo-physical properties of phosphonium-based ILs with different cations and anions. Ferreira et al. [5] focus their study on the transport and thermal properties of several quaternary phosphonium ionic liquids. Beigi et al. [14], Soriano et al. [15], Fernández et al. [16], García-Míaja et al. [17] and Zhang et al. [18] investigate physical and electro-chemical properties of alkyl-imidazolium based ionic liquids. The data studied in these works are experimental measurements of density, dynamic viscosity, refractive index and surface tension as a function of the temperature. Less numerous are studies of thermal conductivity, while no systematic studies are found for electrical conductivity.

In this work, density, refractive index, electrical conductivity, thermal conductivity and dynamic viscosity for five ionic liquids, [P₄₄₄₁]Cl, [P₄₄₄₁][NTf₂], [P₄₄₄₁][MeSO₄], [C₁py][MeSO₄], and [C₄mim][MeSO₄], are experimentally determined from (283.15 to 343.15) K and at atmospheric pressure. Thermal stability of the studied ILs is analyzed by TGA. The selection of liquids in this work is done in order to make a systematic study of the influence of anions and cations on the properties of the liquids. These five ionic liquids can be organized into two groups, one with three ILs containing the same cation,

* Corresponding author.

E-mail address: eva.rodil@usc.es (E. Rodil).

tributylmethylphosphonium ($[P_{4441}]^+$), and another with three ILs containing the same anion, methylsulfate ($[MeSO_4]^-$). Comparisons among those having the same cation or anion are established. For ILs for which literature values of the measured properties are available, a comparison is made to prove that in this study the measurements are correct.

2. Experimental

2.1. Chemicals

The $[C_{1py}][MeSO_4]$ and $[P_{4441}][NTf_2]$ ILs were synthesized in our laboratory as described below. The CAS (Chemical Abstract Service) number, source and grades of the other ILs used in this work are as follows: $[C_4mim][MeSO_4]$ (401788-98-5, Sigma-Aldrich, $\geq 95\%$), $[P_{4441}][Cl]$ (2304-24-7, IoLiTec, $\geq 95\%$) and $[P_{4441}][MeSO_4]$ (34217-64-6, IoLiTec, $\geq 95\%$). In order to minimize the water-content influence in the properties of the pure liquids, all the ILs were dried under vacuum and moderate temperature for 48 h and their water content was determined using a titration method (Metrohm 737 KF coulometer). The water content of the ILs was, in all the cases, lower than 400 ppm. The specifications of the chemicals source are presented in Table 1 and the chemical structures of the ILs are shown in Table S1 in Supporting Information. The structures of prepared and purchased ILs were confirmed by 1H and ^{13}C NMR and the corresponding spectra have been added to Supporting Information, Figs. S1 to S5.

2.1.1. Synthesis of the ionic liquids

The ionic liquid $[C_{1py}][MeSO_4]$ (CAS 37943-43-4) was synthesized by alkylation of pyridine (Riedel-de Hen, $\geq 95\%$) with dimethylsulfate (Aldrich, $\geq 97\%$) as described elsewhere [19]. Pyridine was placed in a round-bottomed flask, with a reflux condenser attached, located in an ice bath to keep the temperature low due to the exothermic character of the reaction. Careful dropwise addition of dimethylsulfate was carried out under Argon atmosphere. Once finished and after melting of the ice and natural warming of the water to room temperature, the flask was placed in an oil bath and heated up to 373 K for 8 h. The resulting mixture, with an ionic liquid appearance, was placed in a rotary evaporator for removal of unreacted materials or other volatile impurities. This removal of volatiles was completed by heating of the mixture at ca. 343 K, with stirring, for 48 h under high vacuum (< 0.1 mbar).

The ionic liquid $[P_{4441}][NTf_2]$ (CAS 324575-10-2) was synthesized via methathetic reaction through $[P_{4441}][MeSO_4]$ (IoLiTec, $\geq 95\%$), following a procedure similar to that described previously [12]. $[P_{4441}][MeSO_4]$ was dissolved in water and mixed with slight excess of an aqueous solution of lithium bis(trifluoromethyl-sulfonyl)imide (Solvionic, $\geq 99\%$), at ambient temperature. Turbidity was observed instantaneously due to the hydrophobicity of the produced IL, however the medium was stirring for at least 4 h. Dichloromethane (Fluka, $\geq 99.9\%$) was added, dissolving the $[P_{4441}][NTf_2]$. This organic phase was then separated and washed several times with fresh water. To separate the dichloromethane, rotary evaporation was used and for the removal of the residual volatile impurities present in the IL, it was connected to a high vacuum line (< 0.1 mbar), while continuous stirring and heating at 343.15 K for at least 48 h.

2.1.2. Characterization of ILs

2.1.2.1. Tributylmethylphosphonium chloride ($[P_{4441}][Cl]$). 1H NMR ($CDCl_3$, 300 MHz) δ_H ppm 0.98 (t, $J = 7.0$ Hz, 9H, $3 \times P(CH_2)_3CH_3$), 1.40–1.70 (m, unresolved, 12H, $3 \times P(CH_2)CH_2CH_2CH_3$), 2.12 (d, $J = 13.5$ Hz, 3H, PCH_3), 2.36–2.58 (m, unresolved, 6H, $3 \times PCH_2$); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ_C ppm 4.8 (d, $J_{P-C} = 52$ Hz, PCH_3), 13.4 ($3 \times P(CH_2)_3CH_3$), 20.0 (d, $J_{P-C} = 49$ Hz, $3 \times PCH_2$), 23.5 (d, $J_{P-C} = 5$ Hz, $3 \times PCH_2CH_2$), 23.7 (d, $J_{P-C} = 16$ Hz, $3 \times PCH_2CH_2CH_3$).

2.1.2.2. Tributylmethylphosphonium bis(trifluoromethylsulfonyl)imide

Table 1
Specification of pure components used in this work.

Chemical name	CAS no.	Source	Purity stated by suppliers (wt%)	Purification method	Purity (wt%)	Analysis method	wH ₂ O (ppm)
Water	7732–18-5	–	–	Distillation	–	–	–
$[P_{4441}][Cl]$	2304–24-7	IoLiTec	> 95	Rotatory evaporator and high vacuum pump	≥ 99	NMR	350
$[P_{4441}][MeSO_4]$	69056–62-8	IoLiTec	> 95	Rotatory evaporator and high vacuum pump	≥ 99	NMR	175
$[C_4mim][MeSO_4]$	401788–98-5	Sigma-Aldrich	≥ 95	Rotatory evaporator and high vacuum pump	≥ 99	NMR	50
$[P_{4441}][NTf_2]$	324575–10-2	Home made	–	Rotatory evaporator and high vacuum pump	≥ 99	NMR	200
$[C_1py][MeSO_4]$	37943–43-4	Home made	–	Rotatory evaporator and high vacuum pump	≥ 99	NMR	50
Dimethyl sulfate	77-78-1	Aldrich	≥ 99.8	none	≥ 99.8	GC ^a	–
Pyridine	110–86-1	Riedel-de Hen	≥ 99.5	none	≥ 99.5	GC ^a	–
Lithium bis(trifluoromethyl-sulfonyl)imide	90076–65-6	Solvionic	≥ 99	none	≥ 99	GC ^a	–
Dichloromethane	75–09-2	Fluka	≥ 99.8	none	≥ 99.8	GC ^a	–
1,2,3-Propanetriol	56-81-5	Fluka	≥ 99.0	none	≥ 99.5	GC ^a	–

^a Gas chromatography.

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