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# Physical properties of the pure 1-methyl-1-propylpyrrolidinium bis(trifluoromethylsulfonyl)imide ionic liquid and its binary mixtures with alcohols

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ABSTRACT

In this paper, experimental densities, speeds of sound, dynamic viscosities, refractive indices and molar isobaric heat capacities of the pure 1-methyl-1-propylpyrrolidinium bis(trifluoromethylsulfonyl)imide ionic liquid, [PMpyr][$NTf_2$], are reported as a function of temperature from $T$ = (293.15 to 343.15) K and at atmospheric pressure. From density and refractive index data, the thermal expansion coefficient, molar refractions and molar refractions for the pure ionic liquid were calculated. Besides, a thermal analysis was carried out for the pure ionic liquid using a differential scanning calorimeter. Linear equations were used to fit the density, speed of sound, refractive index and molar isobaric heat capacity data, while the viscosity data were fitted using common equations such as Arrhenius, Vogel–Fulcher–Tamman (VFT), Litovitz, and fluidity. Furthermore, experimental density, speed of sound and refractive index data for binary mixtures with alcohols and their derived properties (excess molar volume, and excess molar isentropic compression) were determined over the whole composition range from $T$ = (298.15, 303.15 and 308.15) K. The excess properties were satisfactorily fitted by Redlich–Kister equation.



## 1. Introduction

The very low vapor pressure at normal temperature and pressure conditions, the wide liquid range, or the ability to dissolve a large number of substances are some of the properties which make ionic liquids (ILs) very attractive substances. Since two decades ago, ILs are the object of numerous studies about their possible application in industrial processes [1–6]. In order to make this possible, an accurate knowledge about their physical properties, either for pure ILs or mixed with other solvents is very necessary. For example, density is a property required to develop numerous thermodynamic models and to design processes and equipments, while refractive index can be used as a measure of the electronic polarizability of a molecule.

In recent years, a large number of researchers have shown interest in the behavior of the binary mixtures (alcohol + ionic liquid) [7–19]. Until 2010, the most of the studied binary mixtures were those containing ILs with imidazolium cation, specially 1-alkyl-3-methylimidazolium-based ILs with different anions such as chloride, ethylsulfate, trifluoromethanesulfonate, thiocyanate, or tetrafluoroborate [7–13]; although, in recent years, new ILs with other cations like ammonium [15] or pyridinium [18] or isoquinolinium [19] are being studied.

The purpose of this work is the characterization of a new ionic liquid in order to understand the behavior of this pure compound and when it is mixed with alcohols. This information is crucial due to ILs being considered as potential solvents in numerous extraction processes such as mixtures in which alcohols form azeotropic mixtures.

As a continuation of our research concerning physical, thermodynamic, and transport properties of ILs [7–9,20–26], in this work, a thermo-physical study (density, speed of sound, refractive index, viscosity, and molar isobaric heat capacity) for 1-methyl-1-propylpyrrolidinium bis(trifluoromethylsulfonyl)imide, [PMpyr][$NTf_2$], ionic liquid was carried out.

Since one of the most attractive features of these compounds is the wide temperature range within which they are liquid, experimental data included in this work were measured at different temperatures in order to analyze the effect of the temperature on the studied properties. Density, speed of sound, refractive index and molar isobaric heat capacity data were fitted to linear equations while viscosity data were correlated using typical equations like

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Arrhenius [27], Vogel–Fulcher–Tamman (VFT) [28–30], Litovitz [31], and fluidity [32].

The experimental densities and refractive indices of the pure ionic liquid were used to calculate the corresponding thermal expansion coefficient, molar volumes, and molar refractions.

Otherwise, densities, speeds of sound and refractive indices for the binary mixtures {methanol, or ethanol, or 1-propanol + [PMpyr][$NTf_2$]} were also measured at $T$ = (298.15, 303.15 and 308.15) K. From these experimental results, excess molar volumes and excess molar isentropic compressions were calculated and fitted to a Redlich–Kister type equation [33].

To our knowledge, only few density, and viscosity data for the pure [BMpyr][$NTF_2$] ionic liquid were found in literature [34–37], while no data for the binary systems studied in this paper were found in the literature.

## 2. Experimental

### 2.1. Chemicals

Methanol, ethanol and 1-propanol were purchased from Sigma–Aldrich with mass fraction purity higher than 0.999. They were degassed ultrasonically and dried over molecular sieves type $4 \cdot 10^{-8}$ cm, supplied by Aldrich, and kept in bottles under inert atmosphere. The ionic liquid used in this work was acquired at IoLiTec with mass fraction purity higher than 0.99. This compound was dried under vacuum ($p$ = 0.2 Pa) with stirring at moderate temperature ($T$ = 343 K) for at least 48 h, to reduce the water content and volatile compounds to negligible values. The water content for the dried ionic liquid was measured and the obtained value was $431 \cdot 10^{-6}$. All chemicals were always manipulated inside a glove box under an argon atmosphere to avoid water absorption. The purity of the solvents was checked by comparing the experimental density and refractive indices obtained in this work with those found in the literature [34,36,38]. The CAS number, supplier, purity, and physical properties (density and refractive index) of the pure chemicals measured at $T$ = 298.15 K are presented in table 1. Density and refractive index data previously published are also included in this table for comparison purposes. As can be observed from table 1, our experimental density and refractive index values for the pure components agree quite well with literature data.

All binary mixtures were prepared by weighing using a Mettler AX-205 Delta Range balance with an uncertainty of $\pm 3 \cdot 10^{-4}$ g. Special care was taken to avoid variations in composition due to evaporation of solvent or pickup of water by the ionic liquid. For this, all samples were prepared immediately prior to measurements into stoppered bottles inside a glove box, which is under argon atmosphere.

### 2.2. Apparatus and procedure

#### 2.2.1. Densities and speeds of sound

Densities and speeds of sound of the pure ionic liquid were measured using an Anton Paar DSA-5000 digital vibrating-tube densimeter. The DSA-5000 automatically corrects the influence of viscosity on the measured density. The repeatability and uncertainty in experimental measurements have been found to be lower than $\pm(2 \cdot 10^{-6}$ and $3 \cdot 10^{-5})$ g · cm$^{-3}$ for the density and ±(0.01 and 0.3) m · s$^{-1}$ for the speed of sound, respectively. This equipment has a temperature controller that keeps the samples at working temperature with an uncertainty of ±0.01 K. Moreover, the equipment automatically detects the presence of bubbles in the cell. The apparatus was calibrated by measuring the density of Millipore quality water and ambient air according to the manual instructions. The calibration was checked with known density and speed of sound of pure organic compounds.

#### 2.2.2. Refractive indices

To measure refractive indices, an automatic refractometer Abbemat-HP Dr. Kernchen with a resolution of $\pm 10^{-6}$ and an uncertainty in the experimental measurements of $\pm 4 \cdot 10^{-5}$ was used. This equipment also keeps the samples at working temperature with an uncertainty of ±0.01 K. The apparatus was calibrated by measuring the refractive index of Millipore quality water and tetrachloroethylene before each series of measurements, according to manual instructions. The calibration was also checked with known refractive index of pure liquids.

#### 2.2.3. Dynamic viscosities

Kinematic viscosities were determined using an automatic viscosimeter Lauda PVS1 with an Ubbelhode capillary microviscosimeter (Type II; diameter: $1.13 \cdot 10^{-3}$ m) with an uncertainty in experimental measurement of ±0.03 mPa · s. Gravity fall is the principle of measurement on which this viscosimeter is based. The capillary was maintained in a D20KP LAUDA thermostat with an uncertainty of ±0.01 K. The capillary was calibrated and credited by the company. The equipment has a control unit PVS1 (Processor Viscosity System) that is a PC-controlled instrument for the precise measurement of the fall time, using standardized glass capillaries, with an uncertainty of ±0.01 s. In order to verify the calibration, viscosity of pure organic solvents were compared with literature data.

The dynamic viscosity was determined from the following relationship:

$$v = k \cdot (t - y), \tag{1}$$

where $y$ is the Hagenbach correction, $t$ is the flow time, and $k$ is the Ubbelhode capillary viscosimeter constant, being $y$ and $k$ supplied by the company.

**TABLE 1**
CAS number, supplier, purity, density, $\rho$, and refractive index, $n_D$, of pure components at $T$ = 298.15 K.

| Component | CAS number | Supplier | Purity, in mass fraction | $\rho$/(g · cm$^{-3}$) | | $n_D$ | |
|---|---|---|---|---|---|---|---|
| | | | | Exp. | Lit. | Exp. | Lit. |
| Methanol | 67-56-1 | Sigma–Aldrich | >0.999 | 0.78666 | 0.78637[a] | 1.32650 | 1.32652[a] |
| Ethanol | 64-17-5 | Sigma–Aldrich | >0.999 | 0.78548 | 0.78493[a] | 1.35932 | 1.35941[a] |
| 1-Propanol | 71-23-8 | Sigma–Aldrich | >0.999 | 0.79987 | 0.79960[a] | 1.38309 | 1.38370[a] |
| [PMpyr][$NTf_2$] | 223437-05-6 | Iolitec | >0.990 | 1.42786 | 1.4331[$b]<br>1.4304[$c] | 1.42064 | n.a. |

Standard uncertainties $U$ are $U(\rho)$ = 0.00003 g · cm$^{-3}$, $U(n_D)$ = 0.00004 and $U(T)$ = 0.01 K.
[a]Ref. [38].
[b]Ref. [34].
[c]Ref. [36].
n.a.: not available.
[$]Interpolated value from literature data.