

Thermophysical characterization of 1-propylpyridinium 1,1,1-trifluoromethanesulfonate, effect of alkyl chain length of the cation, and anion structure

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ABSTRACT

Ionic liquids have attracted increasing attention as promising alternatives to traditional organic solvents due to their unique properties. Thermophysical properties such as density, speed of sound, refractive index, surface tension, isobaric molar heat capacity, kinematic viscosity, and electrical conductivity were measured for 1-propylpyridinium 1,1,1-trifluoromethanesulfonate over a wide temperature range and at atmospheric pressure. Volumetric properties were also determined at temperatures (283.15 - 338.15) K and at pressures up to 65.0 MPa. From these experimental data, some derived properties were calculated. Moreover, the influence of the chemical structure on these properties was investigated through comparing them with ionic liquids of common anion, ethylpyridinium 1,1,1-trifluoromethanesulfonate and 1-butylpyridinium 1,1,1-trifluoromethanesulfonate and an ionic liquid of common cation, 1-butylpyridinium tetrafluoroborate.

1. Introduction

Ionic liquids (ILs) are salts with a low melting point, which remain liquid near room temperature, typically composed of large organic cations paired with small organic or inorganic anions [1–3]. They have gained considerable interest thanks to their tuneable and desirable properties making them the best replacements of usual solvents [2,4,5].

This extraordinary combination of ions resulting in unique and remarkable properties such as low volatility [4,6–9], non-flammability [4–7], polarity [5], wide solubility [5], high chemical thermal stability and electrochemical stability [4,6,7], non-toxicity [3], high electrical and thermal conductivity [3,4,6–8] has led to numerous applications of these liquids in multidisciplinary areas involving chemistry, electrochemistry, physics, catalysis, analytics, engineering, and biology [3,4,6–8]. For example, ILs have been considered as solvents for reactions [5, 6,8,9], as catalysts [4,5,10] and as lubricants [5]. Also they were used as absorption media for gas, and in extractive distillation for separation purposes [4,6,8,10]. In addition, they were working as heat transfer fluids and in thermal energy systems [3]. Furthermore, they were utilized in processing biomass [9] and as active pharmaceutical ingredients [10]. Since ILs are essentially ionic conductors, they were serving as

innovative electrolytes for electrochemical devices [6] and as operating fluid in a variety of electrochemical applications [9,10]. Additionally, the recent focus on ILs could be attributed to their molecular design, which has been enhanced through the development of new combinations of anions or cations. This has resulted in tailored properties that are ideal for targeted applications [6,7].

As the potential applications of these liquids are expanding, research on ILs is tremendously increasing [8,11]. For a better design and exploitation of these liquids, it is crucial to investigate their basic thermophysical properties, over a wide range of temperatures and pressures [6,8]. The primary objective of this research is to conduct a comprehensive thermophysical study of 1-propylpyridinium 1,1,1-trifluoromethanesulfonate, [ppy][CF₃SO₃]. It is noteworthy to mention that no information regarding this particular ionic liquid can be found in the existing literature.

This study involves experimental measurements of various thermophysical properties such as density, speed of sound, refractive index, surface tension, isobaric molar heat capacity, kinematic viscosity, and electrical conductivity in a wide temperature range and at atmospheric pressure. Furthermore, $p\rho T$ behaviour up to pressures 65.0 MPa has also been studied. Several derived properties, such as isentropic and

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isothermal compressibility, isobaric expansivity, free volume, dynamic viscosity, and molar conductivity were also obtained. The effects of the alkyl chain length of the cation and the anion nature on these properties were both investigated by comparing [ppy][CF₃SO₃] with similar ionic liquids, [epy][CF₃SO₃] [12,13], [bpy][CF₃SO₃] [14,15], and [ppy][BF₄] [15,16]. By making this comparison, a more comprehensive understanding of the relationship between structure and thermophysical property was attained.

2. Experimental

The provenance, purity and water content of the 1-propylpyridinium 1,1,1-trifluoromethanesulfonate [ppy][CF₃SO₃] are listed in Table 1. The ionic liquid was dried for 24 h under high vacuum and at moderate temperature, in order to minimise the water content as much as possible, which was determined using an automatic titrator Crison KF1S-2B. The halide content was estimated by the supplier to be less than 100 ppm. The purity of the sample was checked by NMR by the supplier.

The description of the equipment used to carry out the measurements together with its corresponding calibration has been explained in detail in previous works [12–16]. Here we will mention such equipment together with the uncertainties in the measurements.

An Anton Paar DSA 5000 was used to measure simultaneously density, ρ , and speed of sound, u . The combined expanded uncertainties for these properties, were 10^{-4} g·cm⁻³, and 0.5 m·s⁻¹, respectively, and the standard uncertainty in temperature was 0.001 K. Densities, ρ , as a function of pressure and temperature were measured using an Anton Paar DMA HP cell together with an Anton Paar DMA 5000. The cell temperature is controlled to ± 0.005 K. A hand pump 750.1100 from Sitec was used to provide the pressure. The standard uncertainty in the pressure measurement is 25 kPa. The viscosity of the ionic liquid has influence on the density determination using vibrating tube densimeters [17,18]. So, it is necessary to determine the corresponding viscosity-induced errors, $\Delta\rho$, [15] and then applying these corrections to raw density values. We have followed the suggestion of Sanmamed et al. [19] that estimates the viscosity at a given temperature and pressure using the viscosity at the same temperature and at atmospheric pressure. The final estimated uncertainty of our density measurements is $5 \cdot 10^{-4}$ g·cm⁻³.

The refractive index at a wavelength $\lambda = 589.3$ nm (sodium D line), n_D , was determined with an Abbemat-HP Dr Kernchen refractometer. The combined expanded uncertainty in refractive index was $5 \cdot 10^{-5}$, and the standard uncertainty in temperature was 0.01 K. The surface tension, σ , was measured by means of a Lauda TVT-2 tensiometer. A Lauda E-200 thermostat was used to keep constant the temperature. The combined expanded uncertainty of the measurements was 0.5 mN·m⁻¹, and for temperature the standard uncertainty was 0.01 K. The isobaric molar heat capacity, $C_{p,m}$, was obtained with a TA Instruments DSC Q2000 calorimeter. The combined expanded uncertainty for the isobaric molar heat capacity determinations was 10 J·K⁻¹·mol⁻¹ and the corresponding standard uncertainty for temperature was 0.005 K. The kinematic viscosity, ν , was determined with different Ubbelohde capillaries using a Schoot-Geräte AVS-440 automatic unit. The combined expanded uncertainty for the kinematic viscosity was 1% . The electrical conductivity, κ , at alternating frequency (2 kHz) was measured with a conductimeter Crison LPG31. The proper operation of the conductimeter has been checked by measuring the properties of a reference ionic liquid, 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [20]. Our conductivity results only differ by 1.8% . The combined expanded

uncertainty for the electrical conductivity was 1% . For measuring kinematic viscosities, and electrical conductivities the temperature was kept constant with a Schoot-Geräte CT thermostat (1150/2) with a standard uncertainty in temperature, 0.01 K.

3. Results and discussion

Table S1 of the supplementary material collects the experimental values of density, ρ , speed of sound, u , refractive index, n_D , surface tension, σ , isobaric molar heat capacity, $C_{p,m}$, kinematic viscosity, ν , electrical conductivity, κ and calculated values of isentropic compressibility, κ_S , free volume, f_m , dynamic viscosity, η , and molar conductivity, Λ_m . The preceding calculated properties were obtained from experimental density, speed of sound, refractive index, kinematic viscosity, and electrical conductivity data:

The isentropic compressibility, κ_S , neglecting ultrasonic absorption, from density and speed of sound via Laplace-Newton equation,

$$\kappa_S = 1/(\rho u^2) \quad (1)$$

The free volume, f_m , from density and refractive index, by subtracting the molar refraction, R_m , from the molar volume,

$$f_m = V_m - R_m = V_m(3/(n_D^2 + 2)) \quad (2)$$

The dynamic viscosity, η , from density and kinematic viscosity,

$$h = r \cdot n \quad (3)$$

The molar conductivity, Λ_m , from density and electrical conductivity,

$$L_m = V_m \cdot k \quad (4)$$

The comparison of some of these properties as a function of the temperature at atmospheric pressure of 1-propylpyridinium 1,1,1-trifluoromethanesulfonate with similar ionic liquids, [epy][CF₃SO₃], [bpy][CF₃SO₃], and [ppy][BF₄], are shown in Fig. 1 to Fig. 7.

The effect of temperature and pressure on density, can be evaluated by means of the following properties:

The isobaric expansivity,

$$\alpha_p = 1/V_m \left(\frac{\partial V_m}{\partial T} \right)_p \quad (5)$$

The isothermal compressibility,

$$\kappa_T = -1/V_m \left(\frac{\partial V_m}{\partial p} \right)_T \quad (6)$$

The isobaric expansivity and the isothermal compressibility were obtained by differentiation of the Tait equation used to correlate the densities with temperature and pressure. These isobaric expansivities have been also calculated numerically [21] with similar results.

The corrected densities as a function of pressure and temperature are given in Table S2 of the Supplementary material. Calculated values of α_p and κ_T can be found in Table S3 and Table S4 respectively, of the Supplementary material. All these properties are graphically represented in Fig. 8. On the other hand, the comparison of molar volumes and isothermal compressibilities at one temperature as a function of the pressure of 1-propylpyridinium 1,1,1-trifluoromethanesulfonate with similar ionic liquids are shown in Figs. 9, 10.

The temperature behaviour of most properties at atmospheric pressure is found to be linear. The following equation was used to correlate

Table 1
Ionic liquid.

Chemical name	Molar mass / (g·mol ⁻¹)	CAS number	Source	Purity ^a / (mass fraction)	Water content / (ppm)
1-Propylpyridinium 1,1,1-trifluoromethanesulfonate	271.257	1,242,154-93-3	Iolitec	0.991	80

^a As stated by the supplier by NMR.

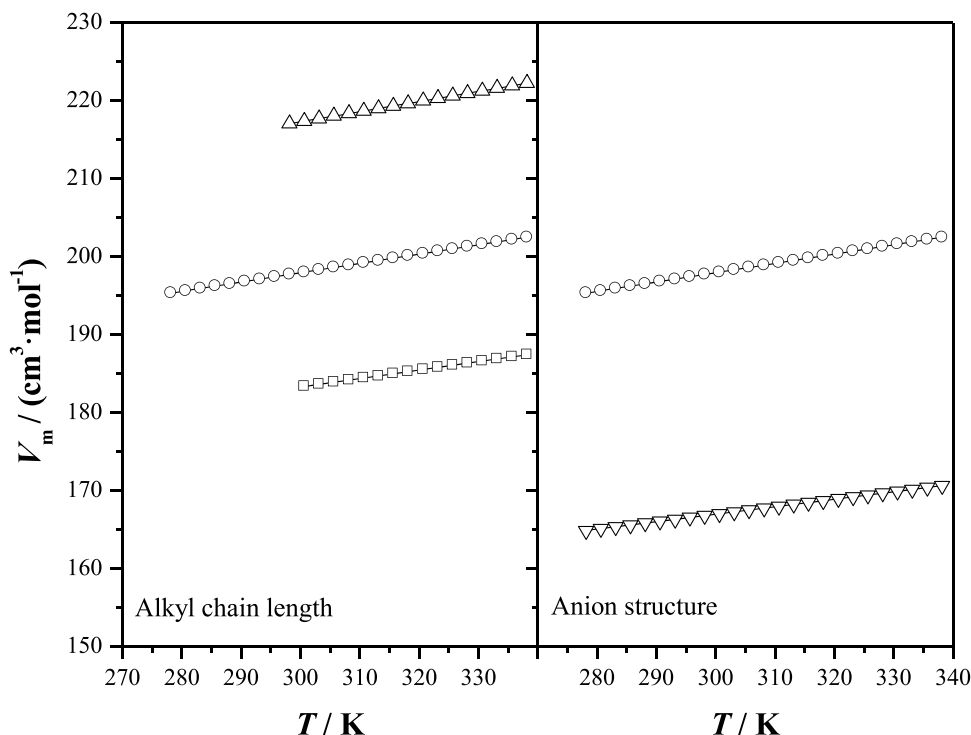


Fig. 1. Molar volume, V_m , of [ppy][CF₃SO₃] as a function of temperature, T , at $p = 0.1$ MPa: (○) experimental values; (—) correlated values; [epy][CF₃SO₃] Ref. [12] (□); [bpy][CF₃SO₃] Ref. [14] (△); [ppy][BF₄] Ref. [16] (▼).

the experimental results with temperature:

$$Y = A \cdot T + B \quad (7)$$

whereas other properties, such as dynamic viscosity and electrical conductivity, have shown a different trend. They were both fitted using the Vogel-Fulcher-Tammann equation [21–24] and Litovitz equation [25]:

$$Y = Y_0 \cdot \exp[B / (T - T_0)] \quad (8)$$

$$Y = A \cdot \exp\left(\frac{B}{T^3}\right) \quad (9)$$

where Y is η or κ , and Y_0 , A , B , and T_0 are adjustable parameters. The fitting parameters, are collected in Table 2 along with the absolute average relative deviations, AARD, obtained by means of the expression:

$$AARD/\% = \frac{100}{n} \sum_{i=1}^n \frac{|Y_{i,exp} - Y_{i,corr}|}{Y_{i,exp}} \quad (10)$$

The Tait equation [26] has been used to correlate the corrected

densities with pressure and temperature:

$$\rho(T, p) = \frac{\rho_0(T, p_0)}{1 - C \times \ln\left(\frac{B(T+p)}{B(T)+p}\right)} \quad (11)$$

$$\rho_0(T, p_0) = \sum_{i=0}^n A_i \cdot T^i \quad (12)$$

$$B(T) = \sum_{i=0}^n B_i \cdot T^i \quad (13)$$

the parameter C was treated as temperature independent, in the above equations the pressure units are MPa and the reference pressure is set to $p_0 = 0.1$ MPa. In Table 3 parameters of the Tait equation together with the corresponding absolute average relative deviation are given.

At constant pressure, a linear increase in molar volume is observed by an increase in temperature, Fig. 1. This can be explained by the thermal expansion of the ionic liquid and the weakening of electrostatic forces between ions as the temperature rises [8]. A comparison of previous results of [epy][CF₃SO₃], [bpy][CF₃SO₃] and [ppy][BF₄] with the studied [ppy][CF₃SO₃] allows us to evaluate the dependence of molar volume upon the cation and anion structure. It was noticed that the cation size influences the molar volume [3,7], more specifically the

Table 2

Fitting parameters, A , B , and C , along with the absolute average relative deviations, AARD, for the measured properties.

Property	A	B	C	AARD /%
ρ / (g·cm ⁻³)	-0.00082	1.61683		0.01
u / (m·s ⁻¹)	-2.2440	2111.49		0.03
η_D	-0.000288	1.542806		0.00
σ / (mN·m ⁻¹)	-0.0482	53.10		0.03
$C_{p,m}$ / (J·K ⁻¹ ·mol ⁻¹)	0.590	230		0.05
η_{VFT}^a / (mPa·s)	0.131	830.85	173.54	0.40
$\Lambda_{m,VFT}^b$ / (mS·cm ² ·mol ⁻¹)	235,574	-695.21	179.18	0.77
η_L / (mPa·s)	0.5375	1.398·10 ⁸		1.21
$\Lambda_{m,L}$ / (mS·cm ² ·mol ⁻¹)	85,195	-1.285·10 ⁸		2.22

^a $A = \eta_0$; $C = T_0$.

^b $A = \kappa_0$; $C = T_0$.

Table 3

Parameters of the Tait equation, A_i , C , and B_i , along with the absolute average relative deviation, AARD.

A_0 / (g·cm ⁻³)	1.61683
A_1 / (g·cm ⁻³ ·K ⁻¹)	-0.00082
C	0.0658
B_0 / (MPa)	199.01
B_1 / (MPa·K ⁻¹)	0.4815
B_2 / (MPa·K ⁻²)	-0.00196
AARD /%	0.02

presence of shorter length of alkyl chain on the pyridinium, contributes to lower molar volume: $[\text{epy}][\text{CF}_3\text{SO}_3] < [\text{ppy}][\text{CF}_3\text{SO}_3] < [\text{bpy}][\text{CF}_3\text{SO}_3]$. This can be explained by the better accommodation and the favourable packing of ions due to a shorter alkyl chain and asymmetry of the cation leading to lower molar volumes [1,27]. With regard to the anion nature, obtained results reveal that $[\text{ppy}][\text{CF}_3\text{SO}_3]$ is denser than $[\text{ppy}][\text{BF}_4]$. In other words, anions with greater molar mass possess higher densities. The same tendency has been found by several authors [6,9,27]. In addition, these results were explained by Bandrés et al. [14], referring to the charge distribution on the anion structure. In fact, the tetrafluoroborate anion has a low surface electrical charge density due to the contribution of highly electronegative fluorine atoms to the distribution of the borate anionic charge. Conversely, the 1,1,1-trifluoromethanesulfonate anion structure exhibits more pronounced anionic charge localization compared to tetrafluoroborate anion, making it an interacting site with the cation. In short, although $[\text{ppy}][\text{CF}_3\text{SO}_3]$ has a higher density than $[\text{ppy}][\text{BF}_4]$, it cannot compensate for its greater molar mass, therefore the molar volume of $[\text{ppy}][\text{CF}_3\text{SO}_3]$ is greater than that of $[\text{ppy}][\text{BF}_4]$.

Finally, the molar volume pressure dependence can be observed from Fig. 9. At a fixed temperature, the molar volume decrease with pressure due to a free volume decrease. Obviously, the differences in molar volume with increasing pressure between the compared ionic liquids are still maintained.

Isobaric expansivity, α_p , refers to the tendency of a material to expand in response to rise in temperature, at constant pressure [28]. According to Fig. 8, isobaric expansivity, α_p , decreases with increasing pressure. But the most interesting feature, the existence of an intersection point of isotherms of α_p , approximately close to 15 MPa. Therefore, we can assume that, the isobaric expansivities, at the corresponding pressure are independent of temperature. Below 15 MPa, higher values of isobaric expansivity were found for higher temperatures. While above this intersection pressure, the isobaric expansivity values decrease with rise of temperature. As stated by Bridgman [29], this point has been noticed before, for many ionic liquids and molecular solvents [30,31], and it can be associated to the minimum of isobaric molar heat capacity

value for the corresponding compound.

Both isentropic compressibility, κ_S , and isothermal compressibility, κ_T , are related with the volume change of a substance, in response to change in pressure, at different conditions, constant entropy, κ_S , and constant temperature, κ_T . Results obtained, Figs. 2, 8 indicate that these properties, κ_T , and κ_S , increase with temperature. On the other hand, isothermal compressibility decreases when pressure rises. From Fig. 2 it is obvious that isentropic compressibility as a function of temperature increases with rising number of carbon alkyl chain in the pyridinium cation following the sequence: $[\text{epy}][\text{CF}_3\text{SO}_3] < [\text{ppy}][\text{CF}_3\text{SO}_3] < [\text{bpy}][\text{CF}_3\text{SO}_3]$. As for the anion nature, higher values of isentropic compressibility were obtained for $[\text{ppy}][\text{CF}_3\text{SO}_3]$ than for $[\text{ppy}][\text{BF}_4]$. The isentropic compressibility is related to the packing arrangement. Thus ionic liquids of shorter alkyl chain, or including smaller anion, are more effectively packed, and will tend to have lower isentropic compressibility. Something similar occurs with respect to isothermal compressibility as a function of pressure, Fig. 10.

Free volume reflects the unoccupied space of ions in the fluid. As it can be seen from Fig. 3 the free volume, f_m , increases with temperature. The free volume values follow the same order if we compare it to isentropic compressibility, higher values were obtained for the cation bearing longer alkyl chain length $[\text{bpy}][\text{CF}_3\text{SO}_3]$, also greater values were observed for $[\text{ppy}][\text{CF}_3\text{SO}_3]$ with respect to $[\text{ppy}][\text{BF}_4]$. Just as the isentropic compressibility or the isothermal compressibility, the ions presenting worse structural fitting or organization inside the fluid have tendency to display higher values of free volume.

Surface tension is the result of different phenomena that occur not only in the surface, but also in the bulk. On the one hand, it could be affected by the preferential orientation of ions and their organization at the surface [32,33]. On the other hand, it depends strongly on the interactions taking place between anion and cation in the bulk [32,33] mainly coulomb and Van der Waals interactions. Fig. 4, shows clearly that the surface tension, σ , exhibits linear decrease with temperature. For ionic liquids having similar anion, the lowering of surface tension follows the order: $[\text{epy}][\text{CF}_3\text{SO}_3] > [\text{ppy}][\text{CF}_3\text{SO}_3] > [\text{bpy}][\text{CF}_3\text{SO}_3]$. Hence this property decreases with an increment of alkyl chain length of

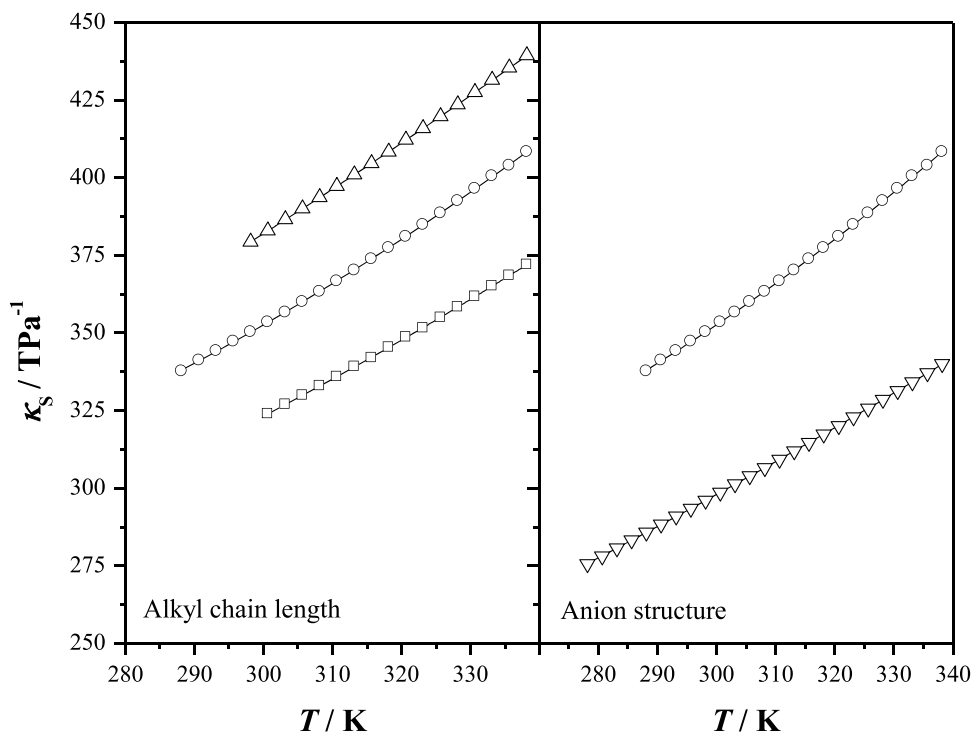


Fig. 2. Isentropic compressibility, κ_S , of $[\text{ppy}][\text{CF}_3\text{SO}_3]$ as a function of temperature, T , at $p = 0.1$ MPa: (○) experimental values; (—) correlated values; $[\text{epy}][\text{CF}_3\text{SO}_3]$ Ref. [12] (□); $[\text{bpy}][\text{CF}_3\text{SO}_3]$ Ref. [14] (△); $[\text{ppy}][\text{BF}_4]$ Ref. [16] (▼).

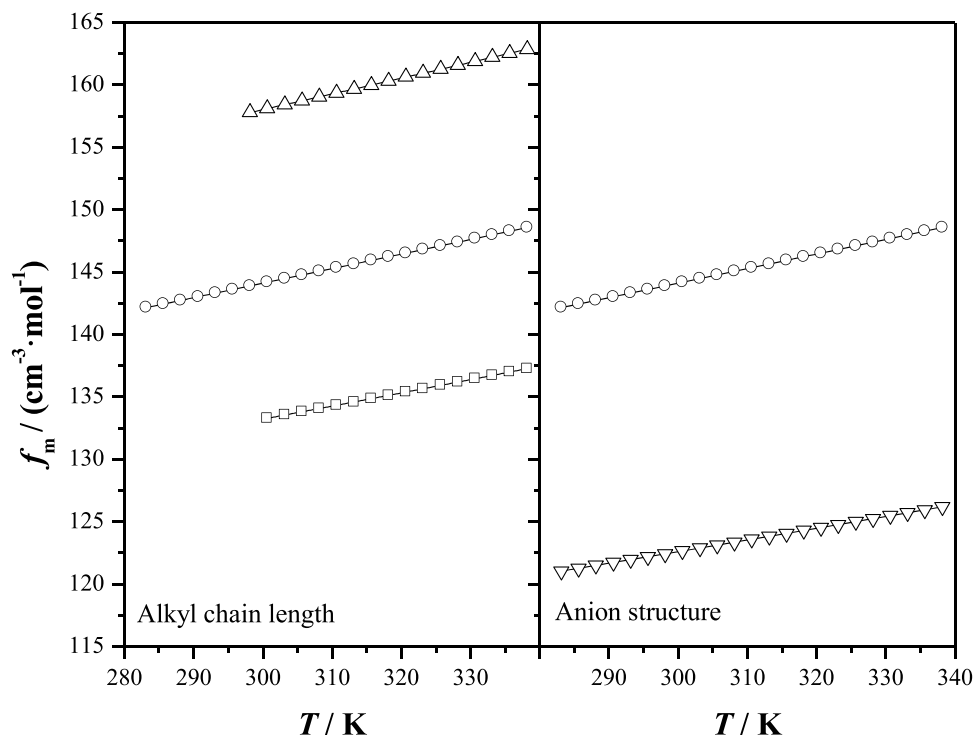


Fig. 3. Free volume, f_m , of [ppy] [CF₃SO₃] as a function of temperature, T , at $p = 0.1$ MPa: (○) experimental values; (—) correlated values; [epy] [CF₃SO₃] Ref. [12] (□); [bpy] [CF₃SO₃] Ref. [14] (△); [ppy] [BF₄] Ref. [16] (▼).

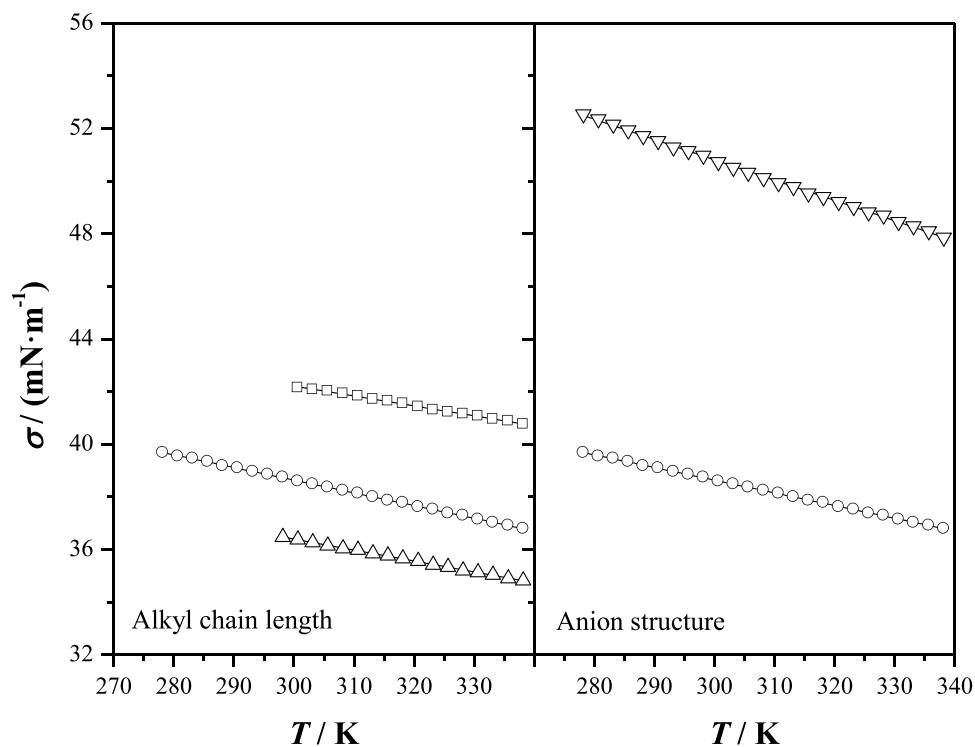


Fig. 4. Surface tension, σ , of [ppy] [CF₃SO₃] as a function of temperature, T , at $p = 0.1$ MPa: (○) experimental values; (—) correlated values; [epy] [CF₃SO₃] Ref. [12] (□); [bpy] [CF₃SO₃] Ref. [14] (△); [ppy] [BF₄] Ref. [16] (▼).

pyridinium. This trend was remarked for other studied ionic liquids [34, 35]. As for ionic liquids owing similar cation, greater values were found for [ppy][BF₄] than for [ppy][CF₃SO₃]. Therefore, we can note that surface tension decreases with increasing anion size, this behaviour was also observed previously [35]. Based on these findings, we can say that

increasing alkyl chain length of the cation contribute to a rise of Van der Waals interactions and to a weakening of the coulomb interactions. Taking into account, that electrostatic contributions are dominating, then it becomes reasonable to obtain lower surface tensions with higher alkyl chains [34]. Moreover, it was specified that complex molecules

such ionic liquids tend to expose their nonpolar parts toward the gas phase [12,35], forming an aliphatic overlayer [34], in order to minimize their surface energies. Whereas polar parts composed here, of the pyridinium rings and the anions are forming another sublayer [34]. Increasing the alkyl chain length will lead to an increase of the distance between polar and non-polar layers and consequently reducing the coulomb interactions. In the same way, an increase of the anion size leads to an overall decrease of electrostatic interaction between cation and anion, leading to lower surface tension values [34]. Furthermore, this behaviour could be attributed to the preferential organization and better confinement of tetrafluoroborate anion in the surface, compared to 1,1,1-trifluoromethanesulfonate one due to its spherical shape [14].

Isobaric molar heat capacity, $C_{p,m}$, is a useful thermodynamic property of fluid related with energy required to increase the temperature of one mole of substance by one degree, at constant pressure [3]. This energy can be accumulated in several modes translational, vibrational and rotational. Hence, bigger molecules will have more energy saving modes and as a result higher heat capacity [9]. Generally, the isobaric molar heat capacities for ionic liquids are larger than usual organic solvents [36]. This property represents also the dependence between energy and temperature for a specified material [36]. According to Fig. 5, isobaric molar heat capacity has a linear trend as a function of temperature, and increases as the temperature rises. An increase in the length of the cation alkyl chain number is reflected in an increase in isobaric molar heat capacity, with [bpy][CF₃SO₃] presenting the highest values. Similarly, the anion structure significantly changes the heat capacity, it is clear that greater values were obtained for the larger anion [ppy][CF₃SO₃], indicating again that this property increases with anion size.

Dynamic viscosity, η , is the most required transport property, which refers to the internal friction of the fluid provoked by intermolecular interactions. It was recognized that viscosity of ionic liquids vary widely depending the type of anion and cation, and it is considerably higher than typical solvents [36]. The influence of temperature on dynamic viscosity for [ppy][CF₃SO₃] is shown in Fig. 6 along with the ionic liquids with which it is compared. For all ionic liquids, dynamic viscosity

markedly decreases as the temperature rises. This could be explained by the better mobility of ions in the fluid, as a result of reducing molecular interaction that block this movement [3]. It is observed that longer alkyl substituents on the cation, display higher dynamic viscosities following the sequence: [epy][CF₃SO₃] < [ppy][CF₃SO₃] < [bpy][CF₃SO₃]. Since viscosity is strongly dependant on intermolecular interactions, higher values of dynamic viscosity could be attributed to stronger Van der Waals interactions for longer alkyl substituents. Similar trends were also found for other ionic liquids [3,28,37]. If we compare both ionic liquids with fixed cation, it is clear that [ppy][BF₄] is more viscous than [ppy][CF₃SO₃]. These results agree with Tokuda et al. [6], who suggested that 1,1,1-trifluoromethanesulfonate anion presents more pronounced charge localization compared to borate anion. Consequently, more interacting sites with the cation, leading to lower ionic concentration and smaller dynamic viscosity values. Moreover, it was stated that ionic liquids including symmetric or spherical anions are more viscous, which is the case for borate anion [36]. These conclusions were also derived by other authors [3,37].

Molar conductivity, Λ_m , is considered as another basic transport property. Using the molar conductivity instead of the conductivity, the effects of molar concentration and density on this property are taken into account, giving a good indication of the number of charge carriers in an ILs [38]. This property is also temperature dependant, and this dependency can be exhibited in Fig. 7. Generally, in the ionic movement, the viscosity, the molar mass and the ion size all have an influence on this magnitude [4,12,37]. It was found that molar conductivity increases exponentially with temperature. This trend could be attributed to the high mobility of ions at higher temperatures. In addition, high dynamic viscosity values lead to low molar conductivity values. As expected the sequence when comparing cation alkyl chain length was inverted: [epy][CF₃SO₃] > [ppy][CF₃SO₃] > [bpy][CF₃SO₃]. So, an increase of the alkyl chain length in the cation increases the dynamic viscosity and decreases the molar conductivity, which agrees with the general behaviour of ionic liquids [12,37,39]. Surprisingly, for the anion effect, it was found that smaller values of molar conductivities obtained for the [ppy][CF₃SO₃] despite having a lower dynamic viscosity values.

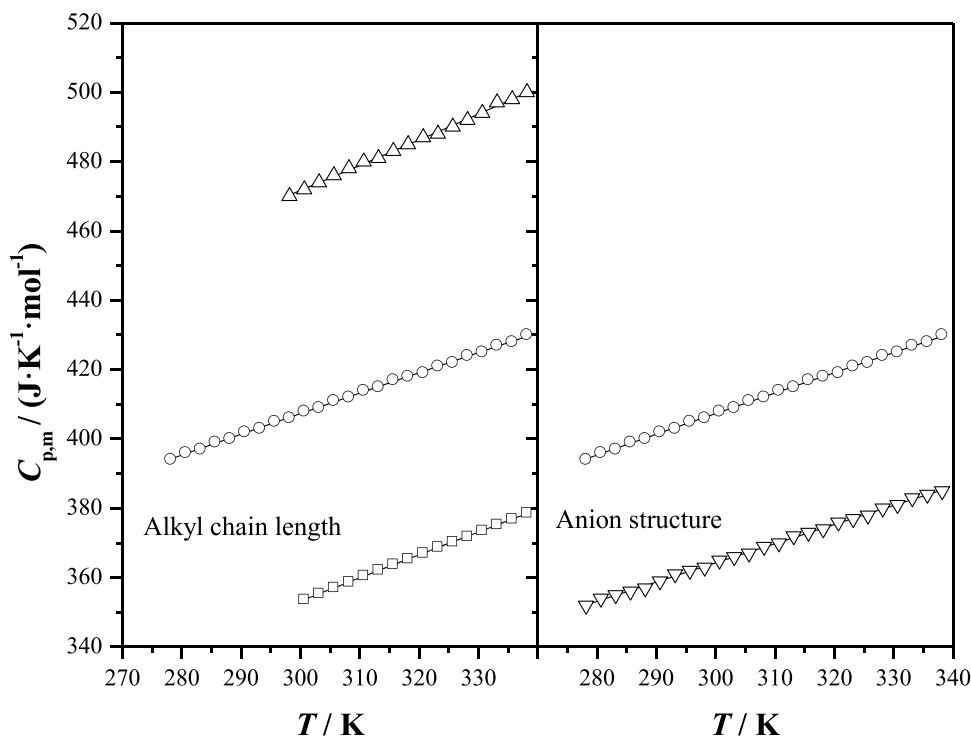


Fig. 5. Isobaric molar heat capacity, $C_{p,m}$, of [ppy][CF₃SO₃] as a function of temperature, T , at $p = 0.1$ MPa: (○) experimental values; (—) correlated values; [epy][CF₃SO₃] Ref. [12] (□); [bpy][CF₃SO₃] Ref. [14] (△); [ppy][BF₄] Ref. [16] (▼).

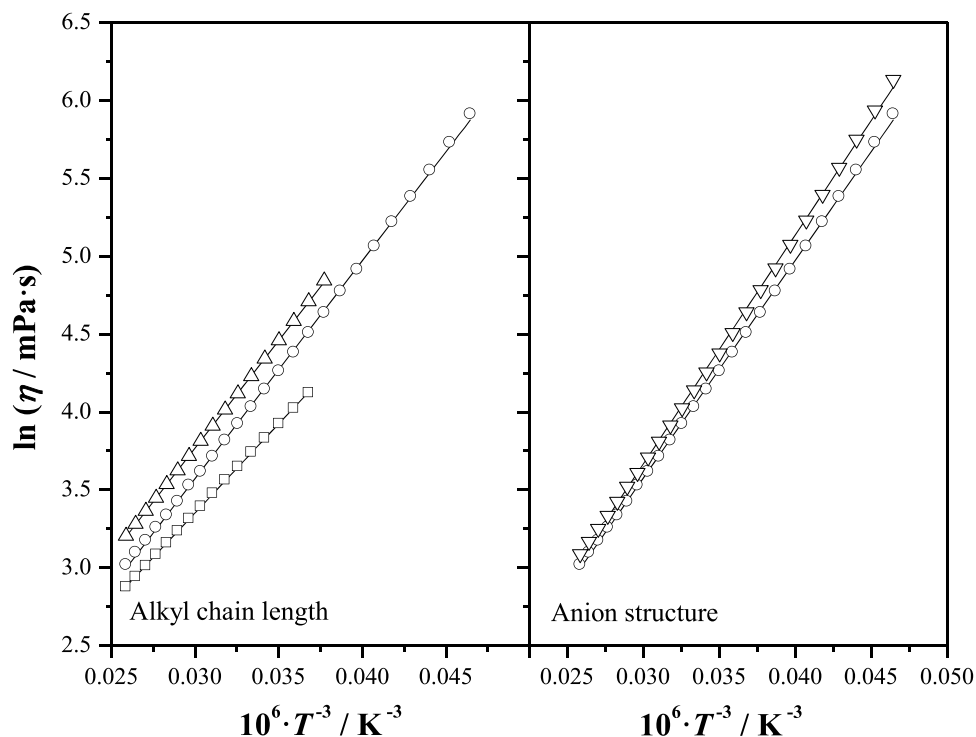


Fig. 6. Litovitz plot ($\ln \eta$ versus $1/T^3$) for dynamic viscosity, η , of [ppy] [CF₃SO₃] as a function of temperature, T , at $p = 0.1$ MPa: (○) experimental values; (—) correlated values; [epy] [CF₃SO₃] Ref. [13] (□); [bpy] [CF₃SO₃] Ref. [14] (△); [ppy] [BF₄] Ref. [16] (▼).

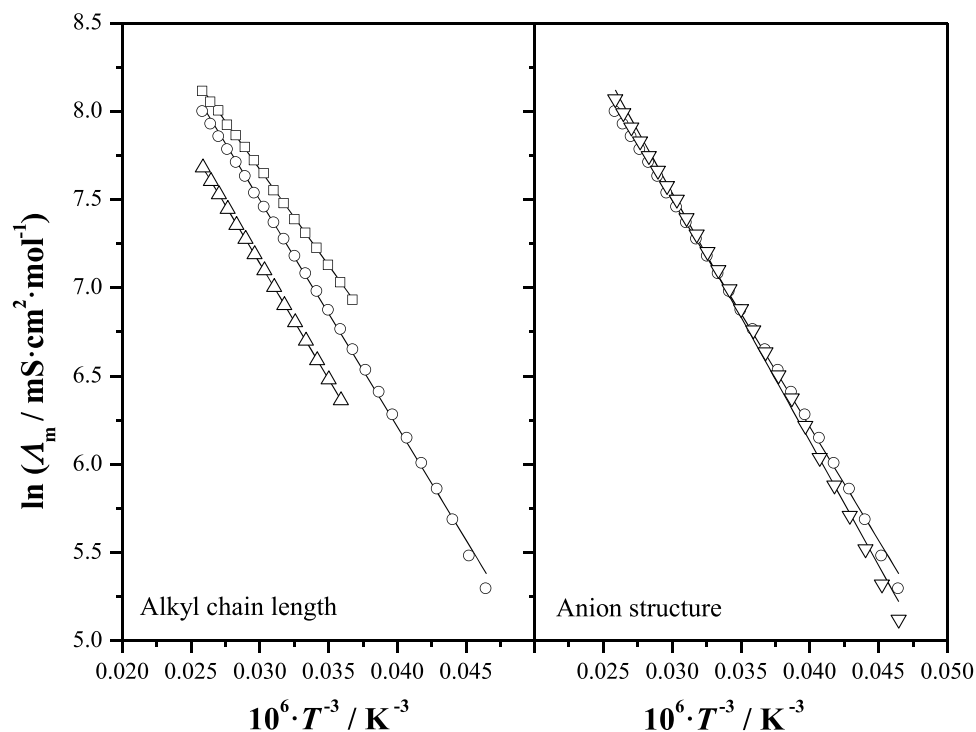


Fig. 7. Litovitz plot ($\ln \Lambda_m$ versus $1/T^3$) for molar conductivity, Λ_m , of [ppy] [CF₃SO₃] as a function of temperature, T , at $p = 0.1$ MPa: (○) experimental values; (—) correlated values; [epy] [CF₃SO₃] Ref. [12] (□); [bpy] [CF₃SO₃] Ref. [14] (△); [ppy] [BF₄] Ref. [16] (▼).

Thus bigger anion size has shown smaller molar conductivity values. This attitude and its opposite were also observed by Vila et al. [39], which indicates that the exact influence of anion is not clear. Moreover, Coadou et al. [4] has distinguished between viscosity which is related to the cohesive energy and conductivity that is affected by the structure,

the interaction and the mobility of ions. The molar conductivity of [ppy] [BF₄] is lower than that of [ppy][CF₃SO₃] up to $T = 303.15$ K and then becomes higher.

The Walden rule [40] relates the molar conductivity and the dynamic viscosity of a solution:

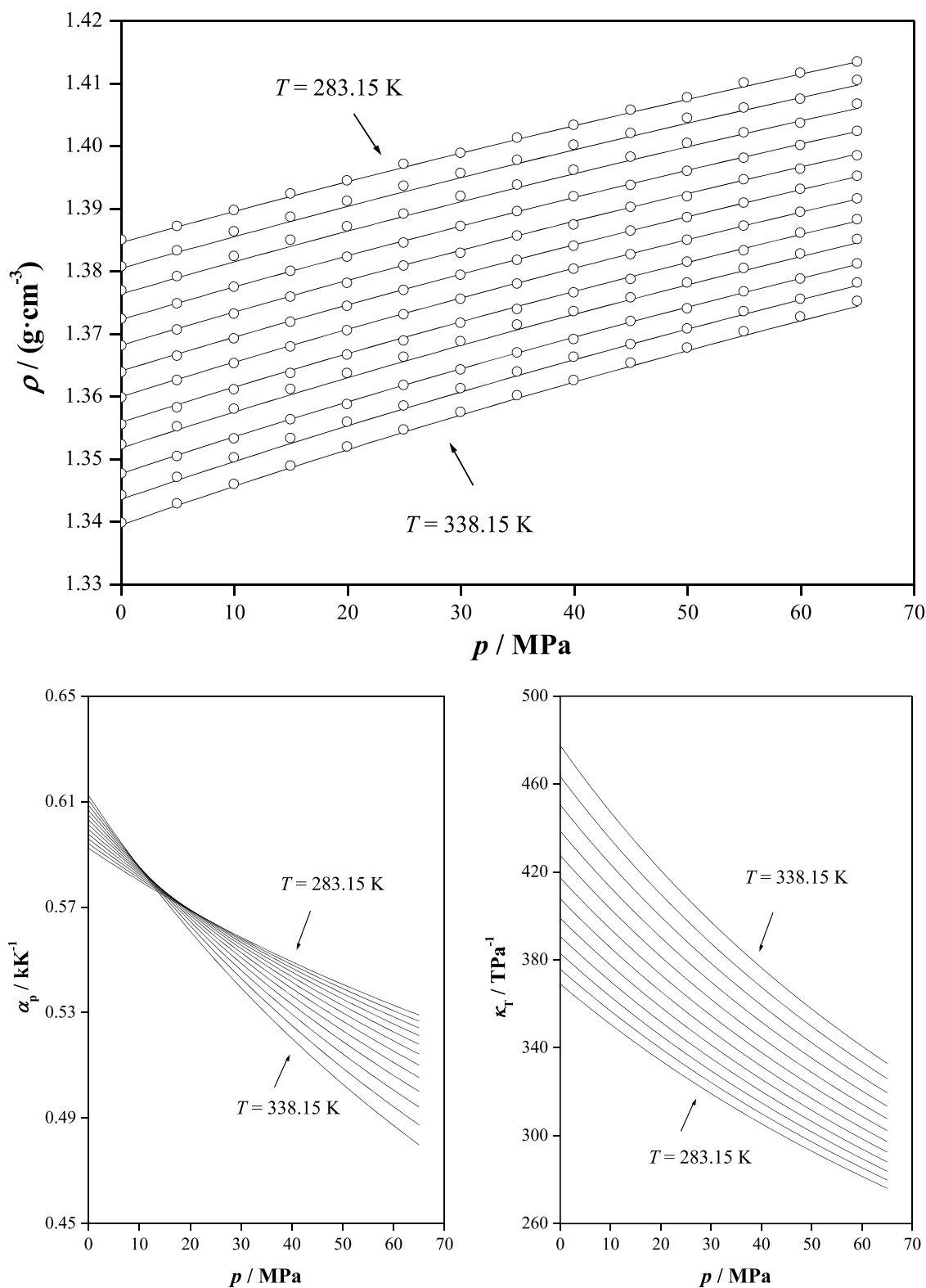


Fig. 8. Density, ρ , isobaric expansivity, α_p , and isothermal compressibility, κ_T , of [ppy] [CF₃SO₃] as a function of temperature and pressure: (○) experimental densities, (—) values calculated with the Tait equation.

$$L_m \cdot h = \text{constant}$$

(14)

this Walden rule also applied well to pure ionic liquids. The ideal line position is fixed using aqueous KCl solutions at high dilution [41,42]. The Walden plot of the studied ionic liquid, [ppy][CF₃SO₃] is presented in Fig. 11. It falls slightly below the ideal Walden line with unit slope, as

the vast majority of ILs [38]. The slope of our Walden plot is 0.9195.

Conclusions

Several thermophysical properties have been experimentally determined to characterize 1-propylpyridinium 1,1,1-

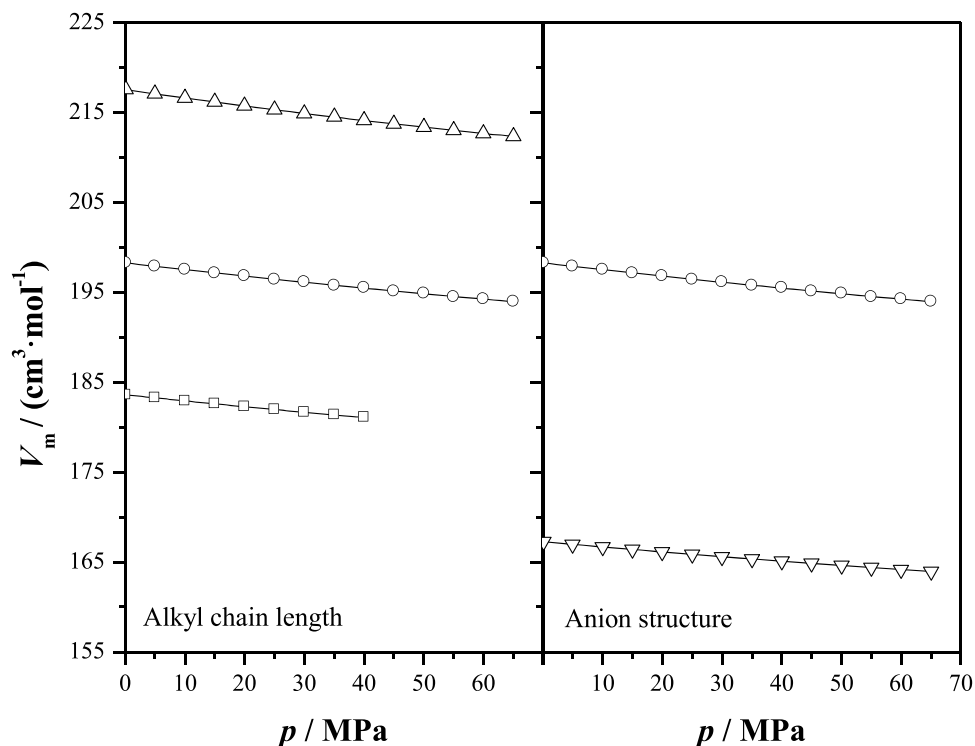


Fig. 9. Molar volume, V_m , of [ppy] [CF₃SO₃] at $T = 303.15$ K as a function of pressure, p : (○) experimental values; (—) correlated values; [epy] [CF₃SO₃] Ref. [12] (□); [bpy] [CF₃SO₃] Ref. [15] (△); [ppy] [BF₄] Ref. [15] (▼).

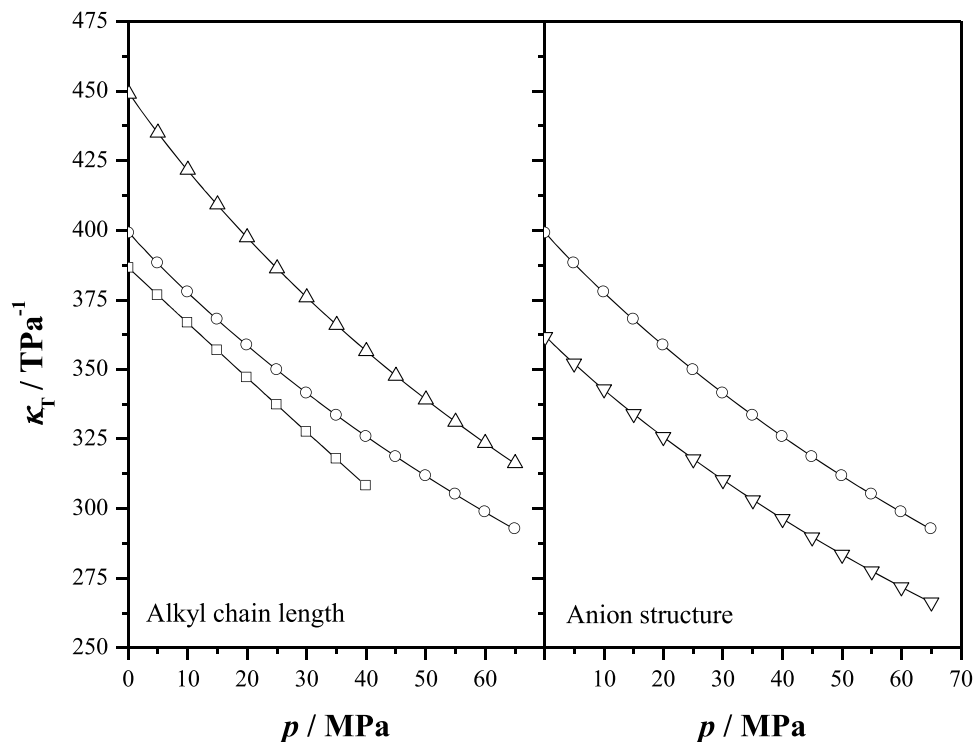


Fig. 10. Isothermal compressibility, κ_T , of [ppy] [CF₃SO₃] at $T = 303.15$ K as a function of pressure, p : (○) experimental values; (—) correlated values; [epy] [CF₃SO₃] Ref. [12] (□); [bpy] [CF₃SO₃] Ref. [15] (△); [ppy] [BF₄] Ref. [15] (▼).

trifluoromethanesulfonate ionic liquid. These properties are density, speed of sound, refractive index, surface tension, isobaric molar heat capacity, kinematic viscosity, and electrical conductivity in a broad range of temperatures at atmospheric pressure. Moreover, the densities

at high pressures, up to 65 MPa, were also determined. Additionally, derived properties, such as isentropic and isothermal compressibility, isobaric expansivity, free volume, and dynamic viscosity were also calculated. Furthermore, similar ionic liquids containing a common

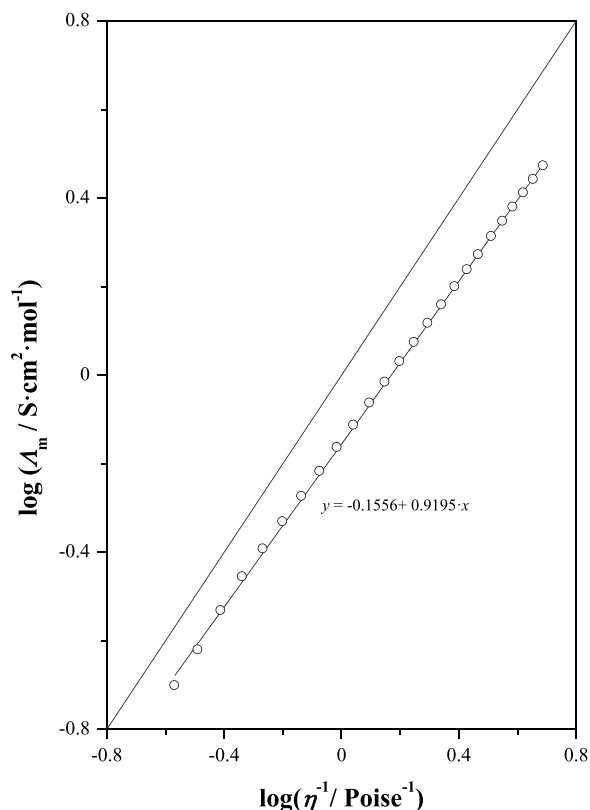


Fig. 11. Walden plot for [ppy] [CF₃SO₃] (○) experimental values.

anion but different alkyl chain length of the cation or a common cation with a different anion were also examined to provide a complete picture of the structure influence on these properties.

From results obtained the following conclusions can be drawn:

Lower molar volumes were obtained for shorter alkyl chain length of the pyridinium cation, and for greater molecular weight for the anion. With respect to isentropic compressibility, the isothermal compressibility, and the free volume, higher values for these properties were observed with longer alkyl chain length of the cation, and for the 1,1,1-trifluoromethanesulfonate anion. Surface tension increases with decreasing alkyl chain length of the cation and with increasing anion size. Isobaric molar heat capacity increases with increasing number of atoms in the cation structure and with larger anion. Finally, regarding transport properties, dynamic viscosity for the ionic liquids having longer alkyl substituents on the cation, display higher dynamic viscosity, on the other hand, [ppy][BF₄] is more viscous than [ppy][CF₃SO₃]. While molar conductivity showed an opposite behaviour.

CRedit author statement

The manuscript was written through contributions of all authors.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.fluid.2023.113900.

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