



Thermophysical properties of pure and water-saturated tetradecyltrihexylphosphonium-based ionic liquids

Catarina M.S.S. Neves, Pedro J. Carvalho, Mara G. Freire, João A.P. Coutinho*

Departamento de Química, CICECO, Universidade de Aveiro, 3810-193 Aveiro, Portugal

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ABSTRACT

In this work, the solubility of water in several tetradecyltrihexylphosphonium-based ionic liquids at 298.15 K, and densities and viscosities of both pure and water-saturated ionic liquids in a broad temperature range were measured. The selected ionic liquids comprise the common tetradecyltrihexylphosphonium cation combined with the following anions: bromide, chloride, bis(trifluoromethylsulfonyl)imide, decanoate, methanesulfonate, dicyanamide and bis(2,4,4-trimethylpentyl)phosphinate. The isobaric thermal expansion coefficients for pure and water-saturated ionic liquids were determined based on the density dependence with temperature. Taking into account that the excess molar volumes of the current hydrophobic water-saturated ionic liquids are negligible, the solubility of water was additionally estimated from the gathered density data and compared with the experimental solubilities obtained. Moreover, the experimental densities were compared with those predicted by the Gardas and Coutinho model while viscosity data were correlated using the Vogel–Tammann–Fulcher method.

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1. Introduction

Ionic liquids (ILs) are widely recognized as promising new solvents for industrial applications. Several processes and products have been developed and are commercially available nowadays [1]. Although most studies in literature address imidazolium-based ILs, the number of industrial applications regarding phosphonium-based ILs is facing a progressive increase. Cytec produces these ILs in bulk quantities; Central Glass Co. Ltd., from Japan, developed pharmaceutical intermediates using phosphonium-based ILs [1]; Texaco used a “ruthenium melt catalyst” dispersed in phosphonium- or quaternary ammonium-based ILs to convert syngas into acetic acid, esters, alcohols and glycol [2]; Rhone-Poulenc used tetrabutylphosphonium chloride to stabilize zero-valent palladium catalysts for carbonylation [2]; and Eastman Chemical Company, one of the oldest examples of the industrial applications of ionic liquids, used a Lewis basic phosphonium iodide IL along with a Lewis acid catalyst for the isomerization of 3,4-epoxybut-1-ene to 2,5-dihydrofuran [1].

The adequate design, optimization and operation of industrial processes involving phosphonium-based ILs require the knowledge of their thermophysical properties, in particular their viscosities and densities. Most of the studies concerning the measurement of thermophysical properties of ILs have been focused on imidazolium- and pyridinium-based ILs [3–9]. However, compared with those nitrogen-based ILs, phosphonium-based salts are less toxic, thermally more stable, readily available in bulk quantities and less expensive [10–12]. Furthermore, unlike the majority of common ILs, most of them are less dense than water [4,13] and more stable towards nucleophilic and basic conditions due to the absence of acidic protons [10]. These characteristics offer greater practicality and scope and have proved to be valuable for specific applications, for instance, in the purification of biomolecules with aqueous two-phase systems [14,15], in the separation of ethanol–water mixtures [16], in the extraction of metals from aqueous phases [17–19], in removing diamondoids from gas condensates and natural gas [20] and in the CO₂ capture and gas separation processes [21–23].

One of the major characteristics inherent to ILs is their high hygroscopicity that is a direct result of their ionic nature. Thus, any large scale application involving ILs must have this issue into account. Most of ILs' thermophysical properties are sensitive to

* Corresponding author. Tel.: +351 234 370200; fax: +351 234 370084.

E-mail address: jcoutinho@ua.pt (J.A.P. Coutinho).

the presence of water and other impurities [24]. The ILs viscosity is one of the properties most affected by the water content [25].

In this work the solubility of water in seven hydrophobic phosphonium-based ionic liquids was determined at 298.15 K. In addition, densities and viscosities of both pure and water-saturated ionic liquids, in a large temperature range and at atmospheric pressure, were measured and reported.

2. Experimental

2.1. Chemicals

The solubilities of water in ILs, densities and viscosities were studied for seven phosphonium-based ionic liquids, namely tetradecyltriethylphosphonium bis(trifluoromethylsulfonyl)imide, [TDTHP][NTf₂] (mass fraction purity > 98%); tetradecyltriethylphosphonium bromide, [TDTHP]Br (mass fraction purity ≈ 96% to 98%); tetradecyltriethylphosphonium chloride, [TDTHP]Cl (mass fraction purity ≈ 93% to 95%); tetradecyltriethylphosphonium decanoate, [TDTHP][Deca] (mass fraction purity ≈ 97%); tetradecyltriethylphosphonium methanesulfonate [TDTHP][CH₃SO₃] (mass fraction purity ≈ 98% to 99%); tetradecyltriethylphosphonium dicyanide, [TDTHP][N(CN)₂] (mass fraction purity ≈ 97%) and tetradecyltriethylphosphonium bis(2,4,4-trimethylpentyl)phosphinate [TDTHP][Phosph] (mass fraction purity ≈ 93%). All ILs were kindly provided by Cytec Industries Inc. The ILs were initially purified by repeatedly washing them with ultra pure water (under constant stirring for a minimum of 24 h). The water used was double distilled, passed by a reverse osmosis system and further treated with a MilliQ plus 185 water purification apparatus. It has a resistivity of 18.2 MΩ · cm and a TOC (Total Organic Carbon content) smaller than 5 μg · dm⁻³. After removing the aqueous-rich phase, the ILs were additionally dried and purified under high vacuum (10⁻³ Pa) and moderate temperature (353 K) for at least 48 h. The purity of each IL was evaluated, after both purification steps, by ³¹P, ¹H, ¹³C, and ¹⁹F NMR spectra. The addition of ultra-pure water for washing, followed by the high vacuum drying procedure, was repeated until no impurities in the ILs were observed as found by NMR analysis. The final purity of all ILs is estimated to be >99 wt%. The water mass fraction contents in the dried ILs, determined with a Metrohm 831 Karl–Fischer coulometer, were 33.6 × 10⁻⁶, (16.0, 28.6, 71.4, 16.3, 15.1) × 10⁻⁵ and 10.8 × 10⁻⁴ for [TDTHP][NTf₂], [TDTHP]Br, [TDTHP]Cl, [TDTHP][Deca], [TDTHP][CH₃SO₃], [TDTHP][N(CN)₂] and [TDTHP][Phosph], respectively. The analyte used for the coulometric Karl-Fischer titration was the Hydranal[®] – Coulomat AG from Riedel-de Haën.

2.2. Apparatus and procedure

2.2.1. Water solubility in ILs

The solubility measurements of water in ILs were performed at 298.15 K and at atmospheric pressure. The IL and water phases were initially vigorously agitated and then allowed to reach saturation equilibrium and complete phase separation, during a period of at least 48 h. This period proved, in previous works [7,26–29], to be the minimum time required to guarantee a complete separation of the two phases and that no further variations in water mole fractions occurred for longer periods. It is safe to admit that after 48 h the saturation values were achieved. The temperature was maintained by keeping the glass vials, containing the phases in equilibrium inside an aluminum block, that is kept inside an air bath, specially designed for this purpose [7,26–29]. A Julabo circulator, model F25-HD, was coupled to the system allowing the passage of a thermostatic fluid around the aluminum block. The system is capable of maintaining the temperature within ±0.01 K by means

of a PID temperature controller driven by a calibrated Pt100 (class 1/10) temperature probe inserted into the aluminum block. The solubility of water in each IL-rich saturated phase was determined using a Metrohm 831 Karl-Fischer (KF) coulometer, where samples of IL rich-phase (≈0.1 g) were taken using glass syringes maintained dry and at the same temperature of the measurements.

2.2.2. Densities and viscosities

Density and viscosity measurements were performed at atmospheric pressure in the temperature range from (278.15 to 363.15) K for the pure ILs, and from (298.15 to 363.15) K for the ILs saturated with water (water saturation at 298.15 K), using an automated SVM 3000 Anton Paar rotational Stabinger viscometer–densimeter. The SVM 3000 Anton Paar rotational Stabinger viscometer–densimeter uses Peltier elements for fast and efficient thermostatisation. Further details regarding the operation system can be found elsewhere [4]. The uncertainty in temperature is within ±0.02 K, the relative uncertainty for the dynamic viscosity is ±0.35% and the absolute uncertainty for the density is ±5 × 10⁻⁴ g · cm⁻³.

3. Results and discussion

3.1. Water solubility in ILs

The solubility of water in ILs, reported in table 1, was measured at 298.15 K. With the exception of [TDTHP][CH₃SO₃], the water solubility in the remaining ILs had previously been reported by us using other ionic liquid samples [27]. As shown in figure 1, the experimental mole fraction solubility data here reported are generally within 1% of the previous data [27] with a maximum deviation of 2.8% observed for the [TDTHP][N(CN)₂] that may be related with the higher purity IL used in this work.

The solubility of water in ILs follows the trend: [TDTHP][Phosph] ≈ [TDTHP][Deca] > [TDTHP][CH₃SO₃] ≈ [TDTHP]Cl > [TDTHP]Br > [TDTHP][N(CN)₂] > [TDTHP][NTf₂], and is in good agreement with the results previously reported [27].

3.2. Density

Among the ILs thermophysical properties, density is particularly widely studied. Nevertheless, data concerning phosphonium-based ionic liquids still remain scarce. Most of the authors focused their studies on the physical properties of imidazolium- [4,25,30,31] and pyridinium-based ILs [8,32], while few researches have centered their attention in phosphonium-based ILs [12,33–38]. Furthermore, few works investigated the influence of water in the physical properties of ILs [4,7,8,25] and, to the best of our knowledge, none has extended these studies to the phosphonium cation family of ILs.

Densities for pure and water-saturated ILs were determined, at atmospheric pressure, in the temperature ranges from (278.15 to 363.15) K and from (298.15 to 363.15) K, respectively. The experimental densities of the pure ILs are reported in table 2 while densities for water-saturated ILs at 298.15 K (see water mole fraction contents in table 1) are reported in table 3.

The experimental density data for the pure ILs reported in this work present relative deviations lower than 3% compared to literature data [12,34–38], as depicted in figure 2. The main exception was observed with the work from Ferguson and Scovazzo [33], where higher relative deviations were obtained. These higher deviations may be a result of different methodologies employed, since the authors determined indirectly the ILs densities by a volumetric method, as well as a result of

TABLE 1
Experimental and calculated, using equations (1) and (2), mole fraction solubilities of water (x_w) in phosphonium-based ILs at 298.15 K.

IL	$x_w \pm \sigma^a$		
	Experimental	Calculated	Relative deviation/%
[TDTHP][NTf ₂]	0.088 ± 0.007		
[TDTHP]Br	0.680 ± 0.030	0.595	12.52
[TDTHP]Cl	0.818 ± 0.022	0.798	2.40
[TDTHP][Deca]	0.872 ± 0.040	0.898	3.05
[TDTHP][CH ₃ SO ₃]	0.825 ± 0.006	0.796	3.49
[TDTHP][N(CN) ₂]	0.496 ± 0.011	0.374	24.59
[TDTHP][Phosph]	0.876 ± 0.001	0.922	5.26

^a Standard deviation of experimental data.

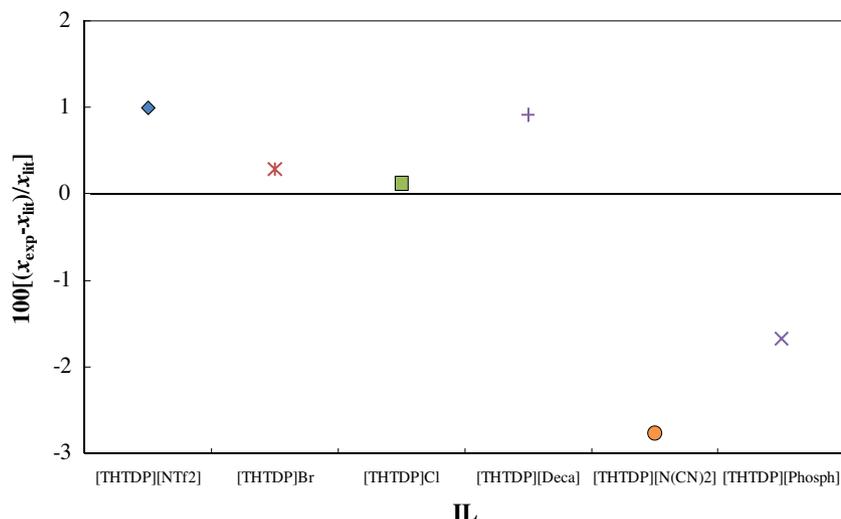


FIGURE 1. Relative deviations between the experimental mole fraction solubilities of water obtained in this work (x_{exp}) and those reported in literature (x_{lit}) [27] at 298.15 K: \blacklozenge , [TDTHP][NTf₂]; *, [TDTHP]Br; \blacksquare , [TDTHP]Cl; +, [TDTHP][Deca]; \bullet , [TDTHP][N(CN)₂]; \times , [TDTHP][Phosph].

TABLE 2

Experimental density, ρ , for pure ILs as a function of temperature and at 0.1 MPa.

T/K	$\rho/(\text{kg} \cdot \text{m}^{-3})$						
	[TDTHP][NTf ₂]	[TDTHP]Br	[TDTHP]Cl	[TDTHP][Deca]	[TDTHP][CH ₃ SO ₃]	[TDTHP][N(CN) ₂]	[TDTHP][Phosph]
278.15	1081.1	967.5	901.6	893.2	940.5	910.8	897.3
283.15	1077.4	964.4	898.6	890.0	937.4	907.8	894.3
288.15	1073.6	961.3	895.7	886.9	934.3	904.9	891.3
293.15	1069.8	958.2	892.8	883.7	931.2	901.9	888.3
298.15	1066.1	955.2	889.9	880.6	928.1	899.0	885.3
303.15	1062.4	952.1	887.0	877.5	925.1	896.1	882.3
308.15	1058.8	949.0	884.0	874.4	922.0	893.3	879.3
313.15	1055.2	946.0	881.1	871.3	918.9	890.4	876.3
318.15	1051.6	942.9	878.2	868.3	915.9	887.6	873.4
323.15	1048.0	939.8	875.3	865.3	912.9	884.8	870.4
328.15	1044.4	936.7	872.3	862.2	909.9	882.0	867.5
333.15	1040.9	933.7	869.5	859.2	907.0	879.2	864.6
338.15	1037.3	930.7	866.6	856.2	904.1	876.4	861.7
343.15	1033.7	927.6	863.7	853.2	901.2	873.7	858.9
348.15	1030.2	924.6	860.8	850.2	898.3	870.9	856.0
353.15	1026.6	921.7	858.0	847.3	895.3	868.1	853.2
358.15	1023.1	918.7	855.1	844.3	892.4	865.3	850.3
363.15		915.7	852.3	841.3	889.4	862.6	847.5

TABLE 3

Experimental density, ρ , for water-saturated ILs (saturation of water at 298.15 K) as a function of temperature and at 0.1 MPa.

T/K	$\rho/\text{kg} \cdot \text{m}^{-3}$						
	[TDTHP][NTf ₂]	[TDTHP]Br	[TDTHP]Cl	[TDTHP][Deca]	[TDTHP][CH ₃ SO ₃]	[TDTHP][N(CN) ₂]	[TDTHP][Phosph]
298.15	1066.1	957.0	901.6	901.2	935.1	900.7	907.3
303.15	1062.4	953.6	898.3	897.8	931.8	897.6	903.9
308.15	1058.7	950.3	895.0	894.5	928.4	894.7	900.5
313.15	1055.0	946.9	891.7	891.1	925.1	891.7	897.2
318.15	1051.4	943.6	888.4	887.7	921.7	888.7	893.8
323.15	1047.7	940.2	885.1	884.3	918.4	885.7	890.4
328.15	1044.0	936.9	881.8	880.9	915.0	882.7	887.1
333.15	1040.4	933.5	878.5	877.5	911.6	879.8	883.6
338.15	1036.7	930.2	875.2	874.0	908.2	876.8	880.2
343.15	1033.1	926.8	871.9	870.6	904.8	873.8	876.8
348.15	1029.6	923.5	868.6	867.1	901.4	870.9	873.4
353.15	1026.0	920.1	865.3	863.7	898.0	867.9	869.9
358.15	1022.4	916.7	862.0	860.2	894.6	865.0	866.5
363.15	1018.8	913.4	858.6	856.8	891.2	862.0	863.1

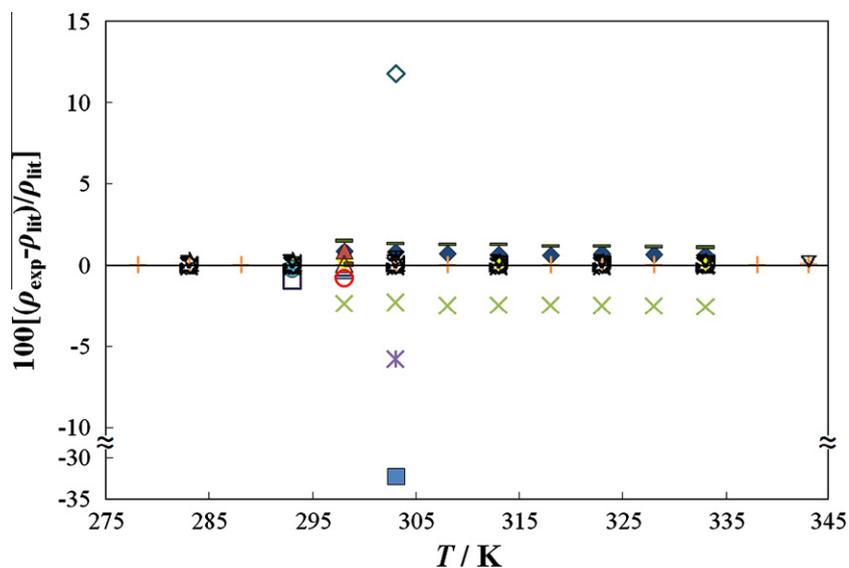


FIGURE 2. Relative deviations between experimental density data obtained in this work (ρ_{exp}) and those reported in literature (ρ_{lit}) as a function of temperature: \blacklozenge , [TDTHP]Cl [34]; \blacksquare , [TDTHP]Cl [33]; \square , [TDTHP]Cl [38]; \blacktriangle , [TDTHP]Cl, Cytec Industries Inc.; \times , [TDTHP][N(CN)₂] [34]; $*$, [TDTHP][N(CN)₂] [33]; \bullet , [TDTHP][N(CN)₂] [12]; $+$, [TDTHP][N(CN)₂] [35]; ψ , [TDTHP][N(CN)₂] [38]; \blacksquare , [TDTHP][N(CN)₂], Cytec Industries Inc.; \blacksquare , [TDTHP][NTF₂] [34]; \diamond , [TDTHP][NTF₂] [33]; \square , [TDTHP][NTF₂] [12]; \blacktriangledown , [TDTHP][NTF₂] [37]; ∇ , [TDTHP][NTF₂] [36]; ζ , [TDTHP][NTF₂] [38]; \triangle , [TDTHP][NTF₂], Cytec Industries Inc.; \blacksquare , [TDTHP][Phosph], Cytec Industries Inc.; \blacktriangle , [TDTHP]Br [38]; \square , [TDTHP]Br, Cytec Industries Inc.; \circ , [TDTHP][Deca], Cytec Industries Inc.; \times , [TDTHP][CH₃SO₃] [38].

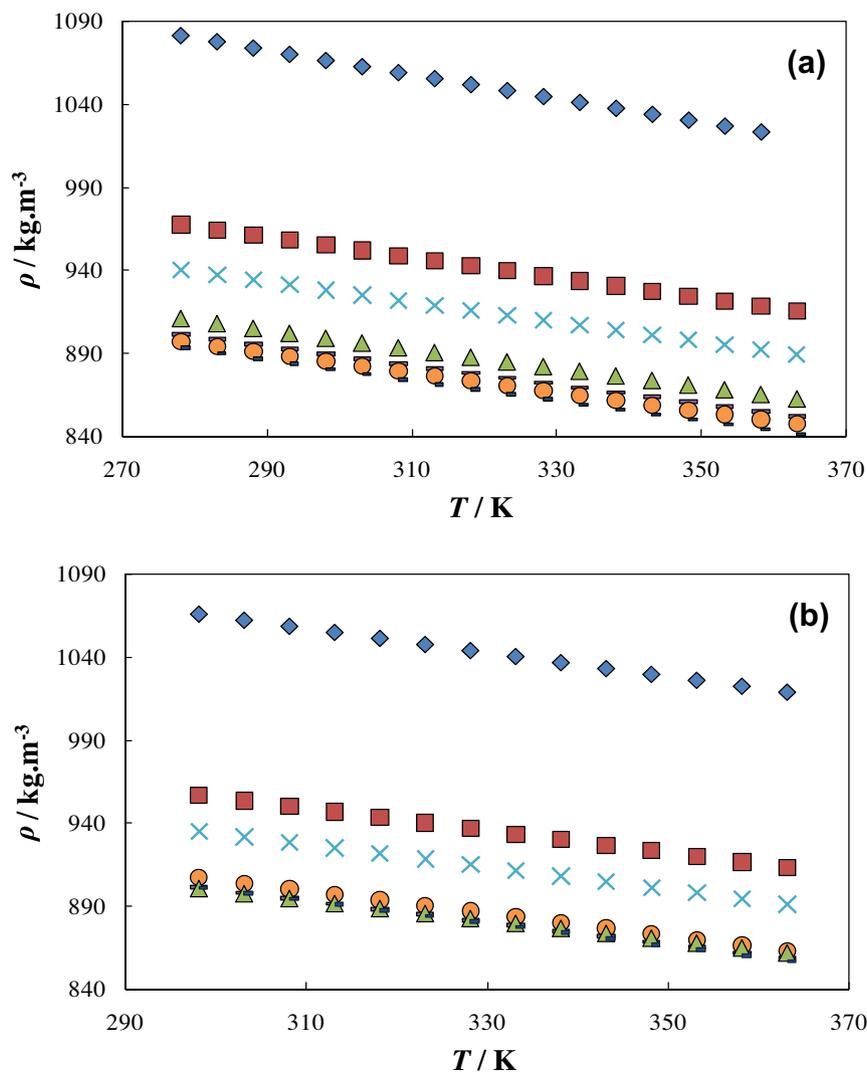


FIGURE 3. Experimental density as a function of temperature and at 0.1 MPa for (a) pure ILs and (b) water-saturated ILs: \blacklozenge , [TDTHP][NTF₂]; \blacksquare , [TDTHP]Br; \times , [TDTHP][CH₃SO₃]; \blacktriangle , [TDTHP][N(CN)₂]; \blacksquare , [TDTHP]Cl; \bullet , [TDTHP][Phosph]; \blacksquare , [TDTHP][Deca].

TABLE 4
Ionic volumes, V , estimated using the Gardas and Coutinho model [39].

Species	$V/\text{\AA}^3$
Cation	
Tetradecyltriethylphosphonium	947 [39]
Anions	
Bis(trifluoromethylsulfonyl)imide	248 [39]
Bromide	36 [38]
Chloride	24 [38]
Decanoate	290
Methanesulfonate	89 [38]
Dicyanamide	72 [38]
Bis(2,4,4-trimethylpentyl)phosphinate	488

the lower purity of the ILs used [33]. Nevertheless, our data present both positive and negative relative deviations to literature indicating that there are no systematic errors in the experimental data here reported.

Figure 3 presents the density results obtained in this work for pure and water-saturated ILs. The density values of pure ILs follow the IL anion trend $[\text{NTf}_2]^- > \text{Br}^- > [\text{CH}_3\text{SO}_3]^- > [\text{N}(\text{CN})_2]^- > \text{Cl}^- > [\text{Phosph}]^- > [\text{Deca}]^-$, while for the water-saturated ILs, the density increases with the anion following order $[\text{NTf}_2]^- > \text{Br}^- > [\text{CH}_3\text{SO}_3]^- > [\text{Phosph}]^- > [\text{N}(\text{CN})_2]^- \approx \text{Cl}^- \approx [\text{Deca}]^-$. With the exception of $[\text{TDTHP}][\text{NTf}_2]$, where the presence of water has a negligible impact in the IL density, the introduction of water leads to an increase in density. Furthermore, more hygroscopic ILs, like $[\text{TDTHP}][\text{Phosph}]$, are more influenced by the presence of water with a relative increase in density in the order of 2.5%.

Assuming that the excess molar volumes are negligible in the narrow composition range of water in the hydrophobic ILs studied, it is possible to estimate the solubility of water in each IL from the densities of the pure and respective water-saturated IL according to the following equations

$$V_{m, \text{mixture}} = V_{m, \text{IL}} \times (1 - x_w) + V_{m, w} \times x_w, \quad (1)$$

$$V_{m, \text{mixture}} = \frac{(1 - x_w) \times Mw_{\text{IL}} + x_w \times Mw_w}{\rho_{\text{mixture}}}, \quad (2)$$

where V_m is the molar volume in $\text{m}^3 \cdot \text{mol}^{-1}$, x_w is the mole fraction saturation of water in the IL, Mw is the molecular weight in $\text{kg} \cdot \text{mol}^{-1}$ and ρ is the density in $\text{kg} \cdot \text{m}^{-3}$. The subscripts IL , w and $mixture$ correspond to the pure ionic liquid, water and to the mixture regarding the IL saturated with water, respectively. Estimated values for the mole fraction of water in the ILs studied at 298.15 K are reported in table 1. The water mole fraction relative deviations between the estimated values using equations (1) and (2), and those determined experimentally range between 2% and 24%. The higher deviations were obtained with the most hydrophobic ILs where the water solubilities are lower and for which the density values do not change significantly in the presence of water. Albeit, this approximation can be used to estimate water saturation values when no experimental data of solubilities are yet available.

The Gardas and Coutinho model [39], an extension of the Ye and Shreeve group contribution method [40], was applied to estimate the pure component density data, accordingly to equation (3),

$$\rho = \frac{Mw}{NV(a + bT + cp)}, \quad (3)$$

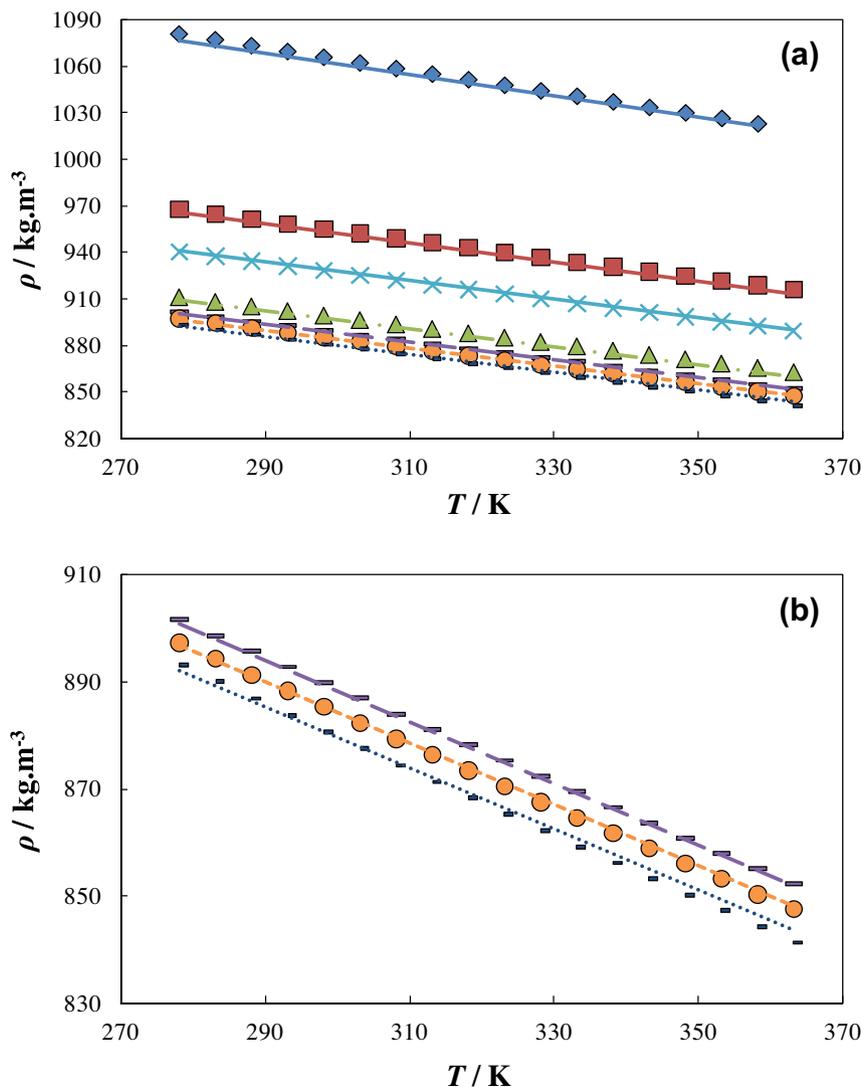


FIGURE 4. Experimental density as function of temperature, and at 0.1 MPa, for the pure ILs (symbols) and respective prediction with the Gardas and Coutinho model [39] (lines): (a) \diamond , —, $[\text{TDTHP}][\text{NTf}_2]$; \blacksquare , —, $[\text{TDTHP}]\text{Br}$; \times , —, $[\text{TDTHP}][\text{CH}_3\text{SO}_3]$; \blacktriangle , - · - ·, $[\text{TDTHP}][\text{N}(\text{CN})_2]$; \blacksquare , - - -, $[\text{TDTHP}]\text{Cl}$; \bullet , - - - ·, $[\text{TDTHP}][\text{Phosph}]$; \blacksquare , · · · · ·, $[\text{TDTHP}][\text{Deca}]$; (b) \blacksquare , - - -, $[\text{TDTHP}]\text{Cl}$; \bullet , - - - ·, $[\text{TDTHP}][\text{Phosph}]$; \blacksquare , · · · · ·, $[\text{TDTHP}][\text{Deca}]$.

TABLE 5Thermal expansion coefficients, α_p , for both pure and water-saturated ILs at 298.15 K and 0.1 MPa.

IL	$10^4 (\alpha_p \pm \sigma^a)/K^{-1}$	
	Pure	Water-saturated
[TDTHP][NTf ₂]	6.788 ± 0.007	6.824 ± 0.005
[TDTHP]Br	6.388 ± 0.006	7.008 ± 0.015
[TDTHP]Cl	6.525 ± 0.007	7.327 ± 0.017
[TDTHP][Deca]	6.922 ± 0.005	7.588 ± 0.027
[TDTHP][CH ₃ SO ₃]	6.464 ± 0.009	7.229 ± 0.022
[TDTHP][N(CN) ₂]	6.292 ± 0.008	6.601 ± 0.081
[TDTHP][Phosph]	6.626 ± 0.007	7.495 ± 0.024

^a Standard deviation.

where ρ is the density in $kg \cdot m^{-3}$, M_w is the IL molecular weight in $kg \cdot mol^{-1}$, N is the Avogadro constant, V is the IL volume in m^3 , T is the temperature in K, and p is the pressure in MPa. The coefficients a , b and c were previously proposed [39] using a broad set of experimental data, and take the values of 0.8005 ± 0.0002 , $(6.652 \pm 0.007) \times 10^{-4} K^{-1}$ and $(-5.919 \pm 0.024) \times 10^{-4} MPa^{-1}$, respectively.

The cation and anion volumes listed in table 4, with the exception of bis(2,4,4-trimethylpentyl)phosphinate and decanoate anions, for which to the best of our knowledge there are no experimental data available in literature, were taken from literature [38,39]. The molar volumes of [Phosph]⁻ and [Deca]⁻ anions were obtained by the fitting of equation (3) to the density data here measured.

The predicted densities for pure ILs are in good agreement with experimental data as shown in figure 4, with a maximum relative deviation of 0.24% observed for [TDTHP][NTf₂]. The Gardas and Coutinho model [39] has shown to be a highly valuable method in the prediction of density data for ILs where no experimental data are available.

TABLE 6Experimental viscosity, η , for pure ILs as a function of temperature and at 0.1 MPa.

T/K	$\eta/(mPa \cdot s)$						
	[TDTHP][NTf ₂]	[TDTHP]Br	[TDTHP]Cl	[TDTHP][Deca]	[TDTHP][CH ₃ SO ₃]	[TDTHP][N(CN) ₂]	[TDTHP][Phosph]
278.15	1246.2	16955	15339	1915.7	7526.5	1646.8	5574.5
283.15	871.17	10457	9447.7	1292.9	4689.7	1144.9	3805.5
288.15	622.45	6688.3	6088.5	902.16	3040.4	816.36	2675.3
293.15	453.64	4421.3	4030.4	644.41	2022.2	592.93	1918.2
298.15	336.74	2988.4	2729.1	471.51	1379.4	438.57	1401.7
303.15	254.24	2065.2	1890.3	352.09	962.83	329.68	1041.5
308.15	195.04	1456.3	1336.4	267.73	686.13	251.71	785.77
313.15	151.85	1046.7	962.50	207.27	498.53	195.00	601.35
318.15	119.85	764.04	705.75	163.00	369.02	153.15	466.24
323.15	95.813	568.06	525.98	130.01	277.77	121.78	365.83
328.15	77.545	428.98	398.19	104.89	212.37	97.961	290.28
333.15	63.470	328.56	305.73	85.752	164.79	79.729	232.76
338.15	52.495	255.03	237.78	70.927	129.63	65.561	188.43
343.15	43.843	200.46	187.39	59.269	103.34	54.428	153.95
348.15	36.953	159.44	149.21	49.987	83.369	45.601	126.77
353.15	31.413	128.21	120.11	42.539	68.008	38.531	105.22
358.15	26.914	104.15	97.659	36.461	56.060	32.848	87.923
363.15		85.436	80.174	31.472	46.650	28.200	73.913

TABLE 7Experimental viscosity, η , for water-saturated ILs (saturation of water at 298.15 K) as function of temperature and at 0.1 MPa.

T/K	$\eta/(mPa \cdot s)$						
	[TDTHP][NTf ₂]	[TDTHP]Br	[TDTHP]Cl	[TDTHP][Deca]	[TDTHP][CH ₃ SO ₃]	[TDTHP][N(CN) ₂]	[TDTHP][Phosph]
298.15	300.01	238.84	134.72	90.951	126.55	190.83	173.82
303.15	224.60	180.54	103.12	70.569	97.432	145.77	128.58
308.15	170.80	138.77	80.197	55.664	76.182	113.30	97.030
313.15	132.06	108.27	63.303	44.650	60.412	89.403	74.519
318.15	103.50	85.713	50.646	36.260	48.539	71.542	58.158
323.15	82.077	68.706	41.047	29.766	39.484	57.961	46.064
328.15	65.746	55.741	33.644	24.651	32.490	47.544	36.996
333.15	53.407	45.715	27.879	20.585	27.021	39.430	30.090
338.15	44.234	37.909	23.333	17.347	22.694	33.031	24.757
343.15	37.137	31.741	19.706	14.722	19.232	27.937	20.592
348.15	31.464	26.817	16.785	12.568	16.448	23.844	17.296
353.15	26.901	22.854	14.399	10.802	14.162	20.518	14.659
358.15	23.172	19.617	12.440	9.3455	12.281	17.781	12.532
363.15	20.092	16.941	10.811	8.1136	10.708	15.513	10.780

The isobaric thermal expansion coefficients (α_p), which considers the volumetric changes with temperature, were calculated using equation (4),

$$\alpha_p = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_p = - \left(\frac{\partial \ln \rho}{\partial T} \right)_p, \quad (4)$$

where ρ is the density in $kg \cdot m^{-3}$, T is the temperature in K and p is the pressure in MPa.

Despite the controversy surrounding the application of a linear correlation or a second order polynomial equation to the density data [8], we have found the use of a linear correlation reasonable to describe the experimental data (in the temperature and pressure ranges investigated in this work). Furthermore, using the law of propagation of errors from the standard deviation coupled to each parameter adjustment, no statistically significant temperature dependence can be assigned to the individual standard deviations of α_p . For that reason, in table 5, α_p is compared for all the ionic liquids investigated at a fixed temperature of 298.15 K. Among the set of ILs investigated, the thermal expansion coefficients are very similar, varying slightly from $(6.292 \text{ to } 6.922) \times 10^{-4} K^{-1}$ for [TDTHP][N(CN)₂] and for [TDTHP][Deca], respectively. The same approach was applied for the water-saturated ILs. Due to the presence of water, the ILs present higher expansion coefficients ranging from $(6.601 \text{ to } 7.588) \times 10^{-4} K^{-1}$ for [TDTHP][N(CN)₂] and for [TDTHP][Deca], respectively.

3.3. Viscosity

It is well established that viscosity is one of the properties most sensitive to the presence of water and other impurities. In a recent paper [9] we have shown that despite the large discrepancies observed among different authors, if an accurate purification procedure and a correct sample manipulation are implemented, similar and accurate viscosity data can be obtained, for the same compounds, even using distinct measurements techniques.

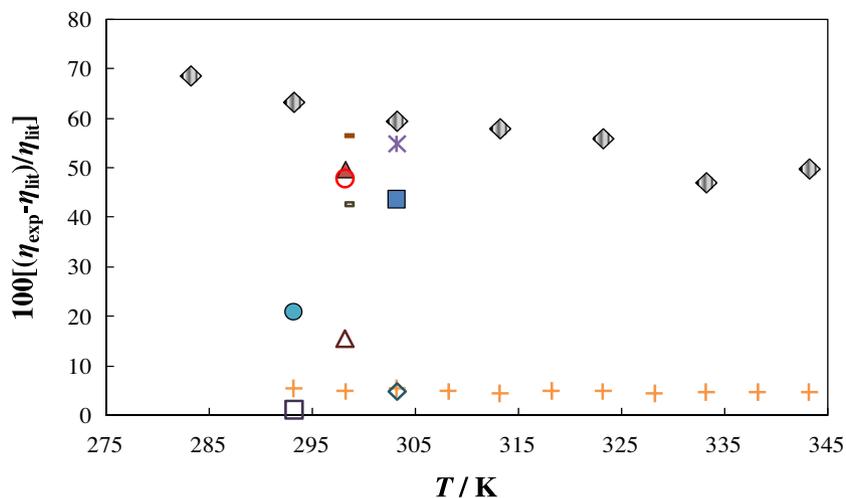


FIGURE 5. Relative deviations between the viscosity experimental data obtained in this work (η_{exp}) and those reported in literature (η_{lit}) as a function of temperature: ■, [TDTHP]Cl [33]; ▲, [TDTHP]Cl, Cytec Industries Inc.; ◊, [TDTHP]Cl [11]; *, [TDTHP][N(CN)₂] [33]; •, [TDTHP][N(CN)₂] [12]; +, [TDTHP][N(CN)₂] [35]; -, [TDTHP][N(CN)₂], Cytec Industries Inc.; ◊, [TDTHP][NTf₂] [33]; □, [TDTHP][NTf₂] [12]; △, [TDTHP][NTf₂], Cytec Industries Inc.; ◻, [TDTHP]Br, Cytec Industries Inc.; ○, [TDTHP][Deca], Cytec Industries Inc.

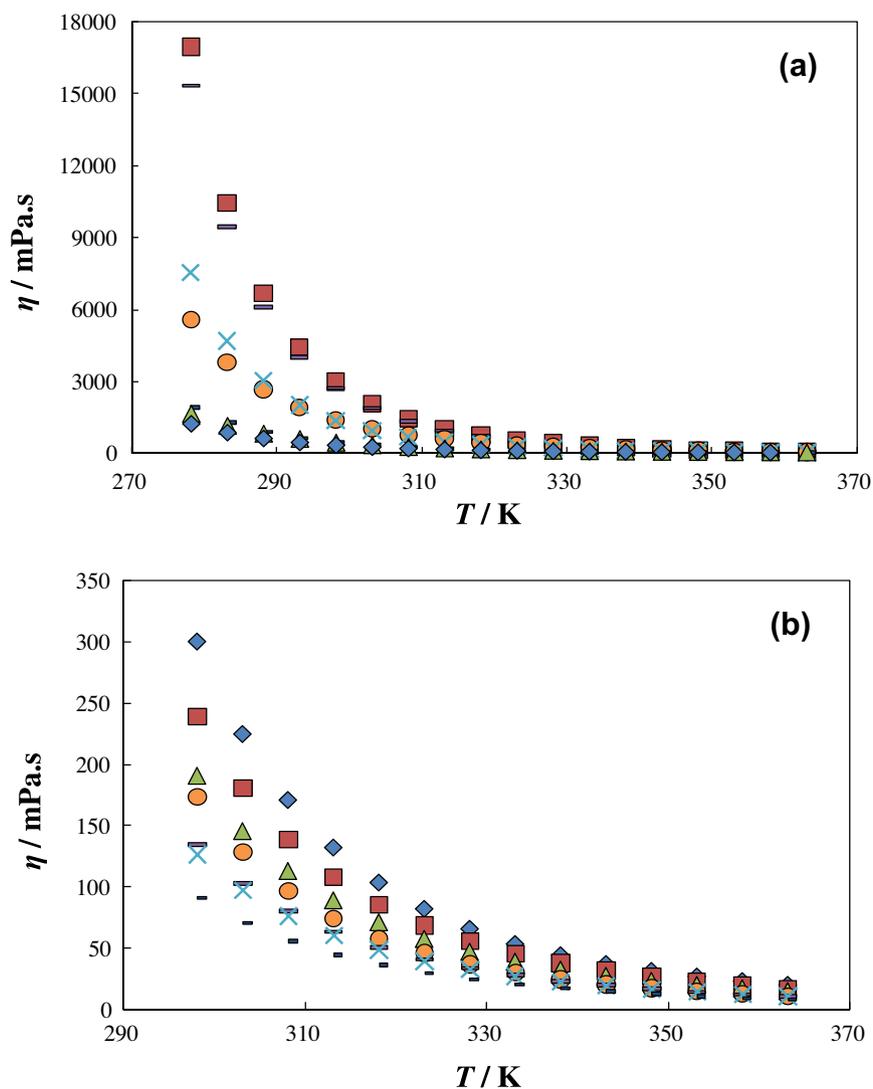


FIGURE 6. Experimental viscosity as function of temperature and at 0.1 MPa for the (a) pure ILs and (b) water-saturated ILs: ♦, [TDTHP][NTf₂]; ■, [TDTHP]Br; ×, [TDTHP][CH₃SO₃]; ▲, [TDTHP][N(CN)₂]; —, [TDTHP]Cl; •, [TDTHP][Phosph]; -, [TDTHP][Deca].

TABLE 8Correlation parameters A_η , B_η and $T_{0\eta}$ obtained from the Vogel–Tammann–Fulcher correlation [41] applied to the experimental data for both pure and water-saturated ILs.

ILs	A_η		B_η/K		$T_{0\eta}/K$	
	Pure	Saturated	Pure	Saturated	Pure	Saturated
[TDTHP][NTf ₂]	-10.402	-9.173	1498.56	1002.99	137.21	172.68
[TDTHP]Br	-11.287	-10.287	1999.85	1350.21	136.59	145.70
[TDTHP]Cl	-11.324	-10.481	1999.82	1300.49	135.90	144.73
[TDTHP][Deca]	-9.605	-11.395	1300.74	1600.22	151.24	120.13
[TDTHP][CH ₃ SO ₃]	-11.227	-10.172	1800.20	1201.71	142.24	149.97
[TDTHP][N(CN) ₂]	-10.599	-10.104	1624.83	1296.28	131.85	144.60
[TDTHP][Phosph]	-10.981	-10.587	2098.81	1250.23	112.74	156.67

The experimental viscosity data for the pure ILs here studied are reported in table 6, and the experimental viscosity data for the water-saturated ILs at 298.15 K are presented in table 7. For the studied compounds, few viscosity data, apart from that reported by the supplier, are available [11,12,33,35]. Furthermore, from the data reported none of the works have implemented an exhaustive purification procedure [11,12,33,35]. Pereiro et al. [35] and Ferguson and Scovazzo [33] purchased the ILs from Cytec Industries Inc. and only applied low vacuum for drying the ILs, while Bradaric et al. [11] and Del Sesto et al. [12] synthesised their own samples implementing a simple degasification step with low vacuum as the main purification procedure. Thus, large discrepancies between the viscosity data measured in this work and those reported in literature [11,12,33,35] would be expected. As

depicted in figure 5, viscosity data for [TDTHP][N(CN)₂], reported by Cytec Industries Inc., and for [TDTHP][Cl], reported by Ferguson and Scovazzo [33], show relative deviations larger than 10%. Nonetheless, viscosity data for [TDTHP][N(CN)₂], reported by Pereiro et al. [35], and [TDTHP][NTf₂], reported by Ferguson and Scovazzo [33] and Del Sesto et al. [12] show relative deviations lower than 5%.

The viscosity describes the internal resistance of a fluid to a shear stress and, as well known, ILs present higher viscosities compared to common volatile molecular solvents. Nevertheless, the ILs high viscosities are also a direct consequence of their high molecular weights. Since viscosity is mainly dependent on intermolecular interactions (H-bonding, dispersive and coulombic interactions), an increase in temperature will substantially decrease the intensity of H-bonding interactions,

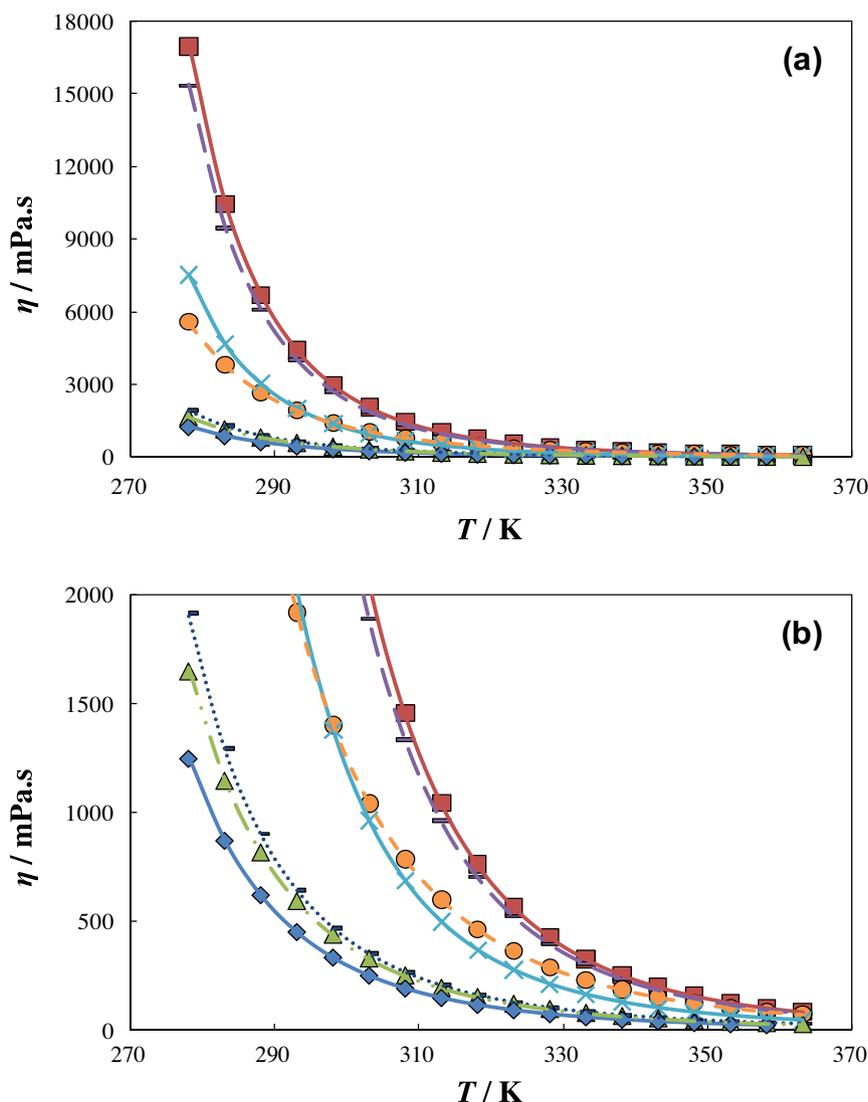


FIGURE 7. Experimental viscosity as function of temperature and at 0.1 MPa for the pure ILs (symbols) and respective correlation using the Vogel–Tammann–Fulcher model (lines): \blacklozenge , —, [TDTHP][NTf₂]; \blacksquare , —, [TDTHP]Br; \times , —, [TDTHP][CH₃SO₃]; \blacktriangle , - · - ·, [TDTHP][N(CN)₂]; \blacksquare , - - -, [TDTHP]Cl; \bullet , - · - ·, [TDTHP][Phosph]; \blacksquare , · · · ·, [TDTHP][Deca].

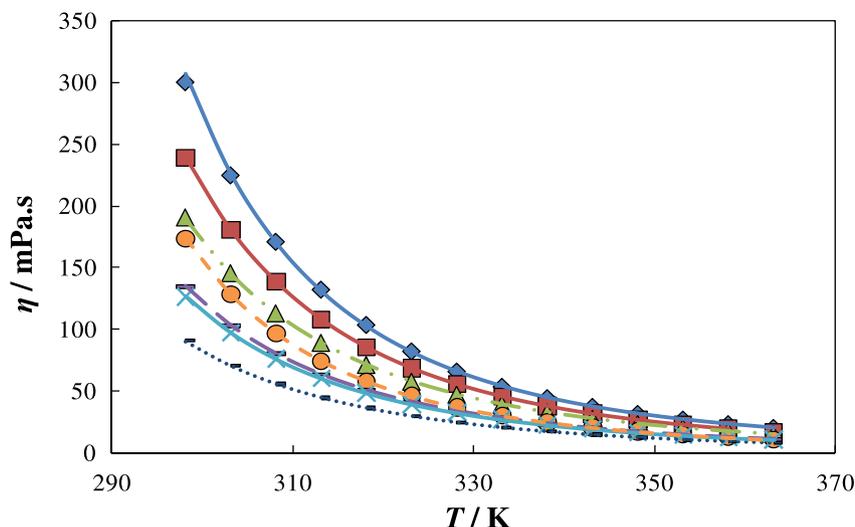


FIGURE 8. Experimental viscosity as function of temperature, and at 0.1 MPa, for the water saturated ILs (symbols) and respective correlation using the Vogel–Tammann–Fulcher model (lines): \blacklozenge , —, [TDTHP][NTf₂]; \blacksquare , —, [TDTHP]Br; \times , —, [TDTHP][CH₃SO₃]; \blacktriangle , - - -, [TDTHP][N(CN)₂]; \blacksquare , - - -, [TDTHP]Cl; \bullet , - - -, [TDTHP][Phosph]; \blacksquare , ·····, [TDTHP][Deca].

and therefore the viscosity. As depicted in figure 6 the viscosity of the pure ILs decreases in the following anion order Br⁻ > Cl⁻ > [CH₃SO₃]⁻ > [Phosph]⁻ > [Deca]⁻ > [N(CN)₂]⁻ > [NTf₂]⁻.

The presence of water has a major impact in viscosities, especially for the less hydrophobic ILs where the water content is significantly higher. The viscosity of water-saturated samples decrease in the following anion order: [NTf₂]⁻ > Br⁻ > [N(CN)₂]⁻ > [Phosph]⁻ > Cl⁻ > [CH₃SO₃]⁻ > [Deca]⁻. The [NTf₂]-based IL shows to be the IL less affected due to the presence of water while [TDTHP][Deca] is the IL that presents the lowest viscosity values. Indeed, these trends are a reflection of the water content on such ILs since [TDTHP][NTf₂] is the most hydrophobic IL studied and [TDTHP][Deca] is at an opposite extreme. Viscosity relative deviations between water-saturated samples and pure ILs present a maximum of 95.06% for [TDTHP]Cl (at 298.15 K), and a minimum of 15.85% for [TDTHP][NTf₂] (at 333.15 K). As can be seen in figure 6, the temperature has also a profound effect on viscosity. However, at higher temperatures not only the viscosity values are very close, but they also seem to be less affected by the presence of water due to the weakening of the H-bonding interactions.

The experimental viscosity data were correlated using the Vogel–Tammann–Fulcher model described in equation (5),

$$\ln \eta = A_{\eta} + \frac{B_{\eta}}{(T - T_{0\eta})}, \quad (5)$$

where η is the viscosity in Pa · s, T is the temperature in K, and A_{η} , B_{η} and $T_{0\eta}$ are adjustable parameters. The adjustable parameters were determined from the fitting of the experimental data using equation (5) for both pure and water-saturated ILs. The fitted constants are presented in table 8.

The correlated viscosities are in good agreement with the experimental data as shown in figures 7 and 8. For the pure ILs a maximum average relative deviation of 0.36% for [TDTHP][CH₃SO₃], and a minimum average relative deviation of 0.16% for [TDTHP][Phosph], were achieved. For the water-saturated ILs maximum and minimum average relative deviations of 0.57% and 0.05% were obtained for the [TDTHP][NTf₂] and [TDTHP]Cl, respectively. Therefore, the Vogel–Tammann–Fulcher model can be an useful interpolative method used for determining viscosities at temperatures not experimentally available.

4. Conclusions

New density and viscosity data for ILs based on the tetradecyltrihexylphosphonium cation in combination with the bis(trifluoromethylsulfonyl)imide, bromide, chloride, decanoate, methanesulfonate, dicyanamide and bis(2,4,4-trimethylpentyl)phosphinate anions are here reported.

For pure ILs the density decrease follows the anions trend: [NTf₂]⁻ > Br⁻ > [CH₃SO₃]⁻ > [N(CN)₂]⁻ > Cl⁻ > [Phosph]⁻ > [Deca]⁻, while viscosity increases as follows: Br⁻ > Cl⁻ > [CH₃SO₃]⁻ > [Phosph]⁻ > [Deca]⁻ > [N(CN)₂]⁻ > [NTf₂]⁻. The presence of water has a marginal effect on the ionic liquid densities yet a large impact through their viscosities. Less hydrophobic ILs are more affected due to

their larger water contents. Moreover, from the density of water-saturated ILs it was proposed a simple method to estimate the water saturation values in each IL at a constant temperature.

The Gardas and Coutinho extension to the Ye and Shreeve group contribution method for predicting density, and the Vogel–Tammann–Fulcher model for correlating viscosity, have shown to be in good agreement with the experimental data, enforcing thus their significance towards the thermophysical data prediction for which no experimental data are yet available.

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