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# Thermophysical Properties of Ammonium-Based Bis{(trifluoromethyl)sulfonyl}imide Ionic Liquids: Volumetric and Transport Properties

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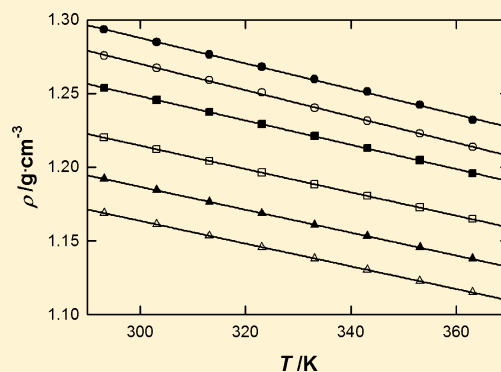
Karolina Machanová,<sup>†</sup> Aurélien Boisset,<sup>‡</sup> Zuzana Sedláková,<sup>†</sup> Mérièm Anouti,<sup>‡</sup> Magdalena Bendová,<sup>\*,†</sup> and Johan Jacquemin<sup>\*,‡,§</sup>

<sup>†</sup>E. Hála Laboratory of Thermodynamics, Institute of Chemical Process Fundamentals AS CR, v. v. i. Rozvojová 135, 165 02 Prague 6 - Suchbát, Czech Republic

<sup>‡</sup>Laboratoire PCMB (E.A. 4244), Université François Rabelais, Equipe CIME, Faculté des Sciences et Techniques, parc de Grandmont, 37200 Tours, France

<sup>§</sup>QUILL Research Centre, Queen's University of Belfast, David Keir Building, Stranmillis Road, Belfast BT9 5AG, Northern Ireland (U.K.)

**ABSTRACT:** Density, rheological properties, and conductivity of a homologous series of ammonium-based ionic liquids *N*-alkyl-triethylammonium bis{(trifluoromethyl)sulfonyl}imide were studied at atmospheric pressure as a function of alkyl chain length on the cation, as well as of the temperature from (293.15 to 363.15) K. From these investigations, the effect of the cation structure was quantified on each studied properties, which demonstrated, as expected, a decrease of the density and conductivity, a contrario of an increase of the viscosity with the alkyl chain length on the ammonium cation. Furthermore, rheological properties were measured for both pure and water-saturated ionic liquids. The studied ionic liquids were found to be Newtonian and non-Arrhenius. Additionally, the effect of water content in the studied ionic liquids on their viscosity was investigated by adding water until they were saturated at 293.15 K. By comparing the viscosity of pure ionic liquids with the data measured in water-saturated samples, it appears that the presence of water decreases dramatically the viscosity of ionic liquids by up to three times. An analysis of involved transport properties leads us to a classification of the studied ionic liquids in terms of their ionicity using the Walden plot, from which it is evident that they can be classified as “good” ionic liquids. Finally, from measured density data, different volumetric properties, that is, molar volumes and thermal expansion coefficients were determined as a function of temperature and of cationic structure. Based on these volumetric properties, an extension of Jacquemin’s group contribution model has been then established and tested for alkylammonium-based ionic liquids within a relatively good uncertainty close to 0.1 %.



## INTRODUCTION

Over the last two decades, replacing volatile organic compounds (VOCs) by less toxic and “greener” solvents is one of the major tasks of chemical engineering. Due to their unique properties, ionic liquids (ILs) are often considered to be such alternatives to VOCs. They are practically nonvolatile, univalent organic salts, mostly liquid at temperatures below 100 °C.<sup>1</sup> Furthermore, a large number of possible combinations of cations and anions allows for a tunability of their properties to specific applications, explaining the reason for coining the term “designer solvents” for ILs.<sup>1–3</sup> As such, ILs are receiving an ever-growing attention as for example promising solvents,<sup>4</sup> reaction media,<sup>5</sup> or entrainers in extractive distillation.<sup>6</sup> The design and optimization of industrial applications using ILs require a good knowledge of thermodynamic and thermophys-

ical properties of pure ILs and their mixtures with molecular solvents. However, reliable data on such properties are still missing to a certain extent, be it due to the diversity and growing number of ILs or because of impurities in samples used in research.<sup>1–3</sup> Even in cases when several data sets of a property are available for a compound, critical assessment using for example a robust gnostic regression method<sup>7,8</sup> appears to be useful.

Our initial research concentrated on developing and studying the relationship between the structure of the cation and anion on their physicochemical properties. Experimental data for

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**Table 1.** Molar Masses ( $M_{II}$ ), Refractive Indices of Dried ILs at 298.15 K, and Water Content in Mass Fractions ( $w_w$ ) and Mole Fractions ( $x_w$ ) of the Dried and Water-Saturated ILs at 293.15 K

IL	purity/mass % <sup>a</sup>	$M_{II}/\text{g}\cdot\text{mol}^{-1}$	$n_D^{298\text{ K}}$	dried IL		water-saturated IL	
				$w_w\cdot 10^3$	$x_w\cdot 10^3$	$w_w\cdot 10^3$	$x_w\cdot 10^3$
[N <sub>6,222</sub> ][Ntf <sub>2</sub> ]	99.5	466.51	1.42599	0.10	2.6	7.45	162.7
[N <sub>7,222</sub> ][Ntf <sub>2</sub> ]	99.5	480.53	1.42708	0.05	1.3		
[N <sub>8,222</sub> ][Ntf <sub>2</sub> ]	99.5	494.56	1.42871	0.05	1.4	6.07	143.5
[N <sub>10,222</sub> ][Ntf <sub>2</sub> ]	99.5	522.61	1.43169	0.04	1.2		
[N <sub>12,222</sub> ][Ntf <sub>2</sub> ]	99.5	550.67	1.43414	0.04	1.2	4.64	124.7
[N <sub>14,222</sub> ][Ntf <sub>2</sub> ]	99.5	578.72	1.43587	0.03	1.0		

<sup>a</sup>NMR analysis carried out by Floris et al.<sup>5</sup>

homologous series of *N*-alkyl-triethylammonium bis-((trifluoromethyl)sulfonyl)imide ILs (abbreviated [N<sub>*n*,222</sub>][Ntf<sub>2</sub>] with *n* = 6, 7, 8, 10, 12, or 14) will be discussed. These ILs were selected because, from an application point of view, they were found to contribute to a better yield of the required enantiomer in stereoselective hydrogenations using a Ru-BINAP catalyst when used as reaction media.<sup>5</sup> Moreover, only scarce data are available in the literature for these ILs. The authors are not aware of any study of this scope on this series of ILs. One work by Kilaru et al.<sup>9</sup> gives values of density of [N<sub>6,222</sub>][Ntf<sub>2</sub>] as a function of temperature; Kilaru and Scovazzo<sup>10</sup> have measured viscosity of [N<sub>6,222</sub>][Ntf<sub>2</sub>] at 30 °C, and Sun et al.<sup>11</sup> give density, viscosity, and conductivity of [N<sub>6,222</sub>][Ntf<sub>2</sub>], [N<sub>7,222</sub>][Ntf<sub>2</sub>], and [N<sub>8,222</sub>][Ntf<sub>2</sub>] at a single temperature.

In this work, volumetric properties, rheological properties, and ionic conductivities in a large range of temperatures and at atmospheric pressure of a homologous series of *N*-alkyl-triethylammonium bis-((trifluoromethyl)sulfonyl)imide were measured. Data on these properties enabled us to have an insight on the overall behavior of ammonium bis-((trifluoromethyl)sulfonyl)imide-based ILs, density, viscosity, and conductivity dependence on the alkyl chain length being an indication of the molecular structure of the studied liquids.

The measured density data enabled us to study the influence of the alkyl chain length on the volumetric properties of studied ILs. Using Jacquemin's modification<sup>12–14</sup> of Rebelo's group contribution model,<sup>15</sup> effective molar volumes of ammonium-based cations and bis-((trifluoromethyl)sulfonyl)imide anion could be obtained. For *N*-alkyl-triethylammonium cations a new relationship was then obtained, describing the dependences of the effective cation volume on the alkyl chain length and on the temperature.

Measurements of flow behavior of selected ILs showed that the studied liquids were Newtonian. Nevertheless the temperature dependence of viscosity shows non-Arrhenius behavior of the measured ILs; hence the Vogel–Tamman–Fülcher-type equation was used. Since water content affects dramatically the viscosity of ILs,<sup>16,17</sup> additional measurements were carried out to quantify the effect of its presence on the viscosity of these hydrophobic ammonium-based ILs.

Finally, the temperature dependence of the ionic conductivity of these ILs has been measured and investigated in detail; as for any electrochemical process, knowledge of the conductivity is essential. Furthermore, reported results enabled us to classify them according to a classical Walden diagram and to evaluate their ionicity.

## EXPERIMENTAL SECTION

**Chemicals Used.** Ionic liquids (ILs) *N*-alkyl-triethylammonium bis-((trifluoromethyl)sulfonyl)imides ([N<sub>*n*,222</sub>][Ntf<sub>2</sub>], where *n* = 6, 7, 8, 10, 12, or 14) were prepared at the Department of Organic Technology, Institute of Chemical Technology Prague (see Floris et al.<sup>5</sup> for details of synthesis and characterization of the studied ILs). Water was purified with a Milli-Q 18.3 MΩ water system.

Prior to use, ILs were dried overnight under vacuum of 0.1 Pa at a temperature of 323.15 K. The water content of the ILs was then determined before and after measurements by coulometric Karl Fischer titration using a Mettler Toledo DL31 titrator. The determination of low water contents (e.g., lower than 100 ppm) was estimated to be within ± 10 %. Refractive indices of pure dried ILs were measured at 298.15 K by a Bellingham and Stanley Abbe refractometer 60/ED with an experimental uncertainty of ± 0.00002.

Water-saturated samples were obtained at 293.15 K by adding water to the conditioned ILs until the appearance of the second (aqueous) phase, after which the water content in each IL was determined by coulometric Karl Fischer titration (see previous work for a description of this methodology<sup>13,17</sup>). Water contents in the saturated samples were found to be determined with an uncertainty of ± 5 %. Molar mass, refractive indices, and water content of the ILs measured in this paper are summarized in Table 1.

**Experimental Equipment.** Two methods of measuring the density were employed during the study, one based on the vibrating tube technique and the other one based on the pycnometry method. An Anton Paar DMA 4500 U-shape vibrating-tube densitometer (QUILL, Belfast) operated in static mode was used at atmospheric pressure. This instrument was fully automated, and therefore, the resonant frequency was automatically determined. The temperature in the cell was regulated within ± 0.01 K using a solid-state thermostat. The measured period of vibration ( $\tau$ ) of the U tube is related to the density ( $\rho$ ) according to:

$$\rho = K\tau^2 + Y \quad (1)$$

where *K* and *Y* are parameters that are function of temperature and pressure. The method described by Lagourette et al.<sup>18</sup> has been used to calibrate the densitometers at temperatures from (293.15 to 363.15) K in 10 K intervals, at atmospheric pressure using air, triply distilled water, and aqueous solutions of NaCl (molalities of 1 mol·L<sup>-1</sup> and 3 mol·L<sup>-1</sup>).<sup>13</sup> At least three independent values were obtained for each temperature.

The densities of pure components were also measured using pycnometers immersed in a thermostatted bath (5 mL, at PCMB, Tours). The temperature was measured using a Pt100

platinum resistance thermometer with an uncertainty of  $\pm 0.1$  K. Prior to measurements, the pycnometer was calibrated using water as a reference.<sup>19</sup> From this study, the uncertainty of density measurements did not exceed  $\pm 0.2$  %.

In each case, the uncertainty of the density measurements was close to  $\pm 10^{-4}$  g·cm<sup>-3</sup>. Furthermore, in light of the comparison of the two data sets obtained in the two laboratories using the same batch of samples, reported results are expected to be accurate within  $\pm 10^{-3}$  g·cm<sup>-3</sup>.

A TA Instruments rheometer AR 1000 was used to determine the rheological behavior and the viscosity ( $\eta$ ) of ILs using a conical geometry. The temperature in the cell was regulated within  $\pm 0.01$  K with a solid-state thermostat. After ensuring that the studied ILs presented a Newtonian behavior, rheograms were recorded at atmospheric pressure as a function of temperature from (293.15 to 368.15) K for dried ILs and from (293.15 to 323.15) K for water saturated ILs, within a shear rate close to 5820 s<sup>-1</sup> or an operating speed of 50 rad·s<sup>-1</sup>. The viscosity standard (Brookfield, 12700 mPa·s at 298.15 K) and water were used to calibrate the rheometer. From this study the uncertainty of viscosity measurements did not exceed  $\pm 1$  %.

Conductivity measurements were performed by using a Crison GLP31 (PCMB, Tours) digital multifrequencies conductometer between (1000 and 5000) Hz. The temperature control at temperatures from (298 K to 420) K was carried out within  $\pm 0.01$  K by means of a JULABO thermostatted bath. The conductometer was first calibrated with standard solutions of known conductivity (i.e., 0.1 mol·L<sup>-1</sup> and 0.02 mol·L<sup>-1</sup> KCl aqueous solutions); the uncertainty of reported conductivities did not exceed  $\pm 2$  %.

## RESULTS AND DISCUSSION

**Density Measurements.** Density measurements of pure ILs were carried out at temperatures ranging from (293.15 to 363.15) K at 0.1 MPa. The experimental data for all pure ILs are reported in Table 2. For the pure ILs, the density values vary typically from (1.16 to 1.30) g·cm<sup>-3</sup> at 293 K and from (1.10 to 1.24) g·cm<sup>-3</sup> at 363 K.<sup>3</sup> As expected, the density is found to decrease with increasing the alkyl chain length on the ammonium cation. Such trends are in good agreement with the variation in density with IL structures previously reported in literature.<sup>3,20</sup> The variation of the density with temperature for the ILs studied is illustrated in Figure 1. A linear equation was used to fit this variation with temperature of the form:

$$\rho_{\text{IL}}(T) = a + b(T) \quad (2)$$

with the parameters  $a$  and  $b$  and standard deviations  $\sigma$  given in Table 3.

Deviations of density values at temperatures from (293.15 to 328.15) K of [N<sub>6,222</sub>][Ntf<sub>2</sub>] given by Kilaru et al.<sup>9</sup> from our data range from (0.03 to 1.7) % in absolute value which may be considered as good agreement considering the high amount of water present in their samples (1080 ppm). Sun et al.<sup>11</sup> give the density of [N<sub>6,222</sub>][Ntf<sub>2</sub>], [N<sub>7,222</sub>][Ntf<sub>2</sub>], and [N<sub>8,222</sub>][Ntf<sub>2</sub>] at 293.15 K that agrees with our data within (0.3 to 1.8) % in absolute value; however, the lack of values at other temperatures as well as that of an experimental uncertainty of density determination in their paper makes the comparison difficult to carry out.

Molar volumes,  $V_{\text{m}}$ , of dried ILs are then calculated as:

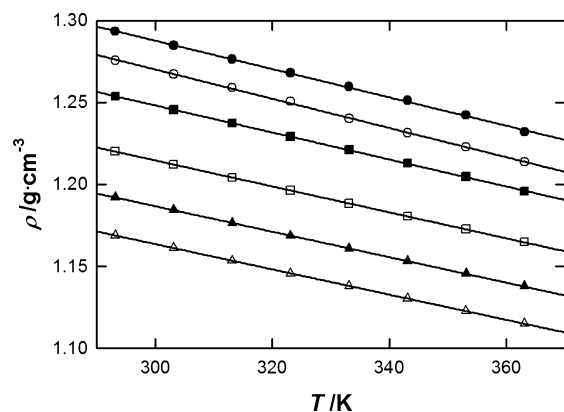
**Table 2. Experimental Densities ( $\rho$ ) and Molar Volumes ( $V_{\text{m}}$ ) of Dried ILs as a Function of Temperature at Atmospheric Pressure**

IL	$T/\text{K}$	$\rho/\text{g}\cdot\text{cm}^{-3}$	$V_{\text{m}}/\text{cm}^3\cdot\text{mol}^{-1}$	
[N <sub>6,222</sub> ][Ntf <sub>2</sub> ]	293.15	1.29332	360.7	
	303.14	1.28487	363.1	
	313.13	1.27645	365.5	
	323.13	1.26809	367.9	
	333.13	1.25973	370.3	
	343.13	1.25121	372.8	
	353.14	1.24223	375.5	
	363.15	1.23200	378.7	
	[N <sub>7,222</sub> ][Ntf <sub>2</sub> ]	293.16	1.27574	376.7
		303.15	1.26736	379.2
313.15		1.25898	381.7	
323.15		1.25066	384.2	
333.15		1.24012	387.5	
343.15		1.23143	390.2	
353.11		1.22291	392.9	
363.15		1.21377	395.9	
[N <sub>8,222</sub> ][Ntf <sub>2</sub> ]		293.18	1.25380	394.4
		303.16	1.24560	397.0
	313.15	1.23740	399.7	
	323.14	1.22924	402.3	
	333.14	1.22109	405.0	
	343.12	1.21296	407.7	
	353.11	1.20471	410.5	
	363.12	1.19581	413.6	
	[N <sub>10,222</sub> ][Ntf <sub>2</sub> ]	293.15	1.22027	428.3
		303.13	1.21226	431.1
313.13		1.20421	434.0	
323.13		1.19624	436.9	
333.13		1.18834	439.8	
343.12		1.18049	442.7	
353.12		1.17266	445.7	
363.12		1.16481	448.7	
[N <sub>12,222</sub> ][Ntf <sub>2</sub> ]		293.16	1.19221	461.9
		303.14	1.18437	464.9
	313.14	1.17646	468.1	
	323.13	1.16861	471.2	
	333.13	1.16083	474.4	
	343.12	1.15311	477.6	
	353.15	1.14543	480.8	
	363.12	1.13783	484.0	
	[N <sub>14,222</sub> ][Ntf <sub>2</sub> ]	293.15	1.16897	495.1
		303.13	1.16122	498.4
313.13		1.15342	501.7	
323.13		1.14566	505.1	
333.12		1.13796	508.6	
343.12		1.13030	512.0	
353.13		1.12271	515.5	
363.13		1.11505	519.0	

$$V_{\text{m,IL}} = \frac{M_{\text{IL}}}{\rho_{\text{IL}}} \quad (3)$$

where  $M_{\text{IL}}$  and  $\rho_{\text{IL}}$  are the molar mass and the density of the studied IL, respectively.

Calculated molar volumes are reported in Table 2 as function of temperature up to 363.15 K. In this study, it appears that the molar volumes of the ILs increase with the temperature and the alkyl chain length on the cation.



**Figure 1.** Experimental densities of dried ILs as a function of the temperature at 0.1 MPa. Effect of the cation alkyl chain length on the densities of [Ntf<sub>2</sub>]<sup>-</sup> based ILs: ●, [N<sub>6,222</sub>]<sup>+</sup>; ○, [N<sub>7,222</sub>]<sup>+</sup>; ■, [N<sub>8,222</sub>]<sup>+</sup>; □, [N<sub>10,222</sub>]<sup>+</sup>; ▲, [N<sub>12,222</sub>]<sup>+</sup>; △, [N<sub>14,222</sub>]<sup>+</sup>. The lines correspond to the fit of the data by eq 2 reported in Table 3.

**Table 3. Correlation Parameters *a* and *b* and Standard Deviation,  $SD_{\rho}^a$ , of Equation 2 for the Density of Dried ILs as a Function of Temperature Determined from Measurements between (293.15 and 363.15) K**

IL	<i>a</i> /g·cm <sup>-3</sup>	10 <sup>4</sup> · <i>b</i> /g·cm <sup>-3</sup> ·K <sup>-1</sup>	10 <sup>4</sup> ·SD <sub>ρ</sub> /g·cm <sup>-3</sup>
[N <sub>6,222</sub> ][Ntf <sub>2</sub> ]	1.54730	-8.649	7
[N <sub>7,222</sub> ][Ntf <sub>2</sub> ]	1.53790	-8.922	6
[N <sub>8,222</sub> ][Ntf <sub>2</sub> ]	1.49559	-8.244	2
[N <sub>10,222</sub> ][Ntf <sub>2</sub> ]	1.45238	-7.923	1
[N <sub>12,222</sub> ][Ntf <sub>2</sub> ]	1.42011	-7.779	1
[N <sub>14,222</sub> ][Ntf <sub>2</sub> ]	1.39472	-7.705	1

<sup>a</sup>SD<sub>ρ</sub> = ((∑(ρ<sub>i</sub><sup>exp</sup> - ρ<sub>i</sub><sup>cal</sup>)<sup>2</sup>)/(n - ν))<sup>0.5</sup> where *n* is the number of experimental points and ν the number of adjustable parameters.

This result is in good agreement with results already available in literature.<sup>3,13,20,21</sup> Furthermore, Rebelo et al.<sup>15</sup> have shown that it was possible to calculate, at 298.15 K and at atmospheric pressure, the molar volume of IL as:

$$V_m = V_c^* + V_a^* \quad (4)$$

where  $V_c^*$  and  $V_a^*$  are the cation and anion effective molar volumes respectively at 298.15 K.

In this case, the mixture of anion and cation is considered to be ideal. This calculation is based on the previous knowledge of the effective molar volume of one ion (anion or cation). The effective molar volume of the other counterion is then obtained by a simple subtraction from eq 4. For example Rebelo et al.<sup>15</sup> have chosen the volume of the [PF<sub>6</sub>]<sup>-</sup> anion as the reference effective molar volume. Its effective molar volume was calculated using the P-F bond length<sup>22</sup> and the van der Waals radius of the fluoride ion<sup>22</sup> yielding a  $V_{[PF_6]^-}^*$  of 73.71 cm<sup>3</sup>·mol<sup>-1</sup> at 298.15 K and at 0.1 MPa. Moreover, the alkyl chain length effect was determined by the following relation for the cation [C<sub>*n*</sub>mim]<sup>+</sup>:

$$V_{[C_n\text{mim}]^+}^* = V_{[\text{mim}]^+}^* + n\alpha^* \quad (5)$$

with  $\alpha^*$  corresponding to the effective molar volume of a CH<sub>2</sub> group in the 1-alkyl-3-methylimidazolium cation at 298.15 K, and *n* is the number of CH<sub>2</sub> groups in the alkyl chain.<sup>13</sup>

The originality of Jacquemin's work is to extend the Rebelo's observation<sup>15</sup> as a function of temperature<sup>12,13</sup> and then of the

pressure,<sup>14</sup> by using in the case of imidazolium-based ILs the following equations:

$$V_m(T^*, p) = [V_{[\text{mim}]^+}^*(T^*, p) + n\alpha^*(T^*, p)] + V_a^*(T^*, p) \quad (6)$$

$$V_{[\text{mim}]^+}^*(T^*, p) = \sum_{i=0}^2 C_i(T^*)^i \quad (7)$$

where  $T^* = T - 298.15$ ,  $\alpha^*$  is the contribution to the molar volume of a CH<sub>2</sub> group on the alkyl chain in imidazolium cation and *n* is the number of CH<sub>2</sub> groups in the alkyl chain, and  $C_i$  is the effective molar volume group contribution parameters described by Jacquemin et al.<sup>12-14</sup>

The effective molar volumes of each studied cation as a function of temperature were estimated by using directly eq 4 and the [Ntf<sub>2</sub>]<sup>-</sup> effective molar volume from Jacquemin et al.<sup>13</sup> Table 4 lists  $C_i$  parameters calculated subsequently using eqs 4 and 7.

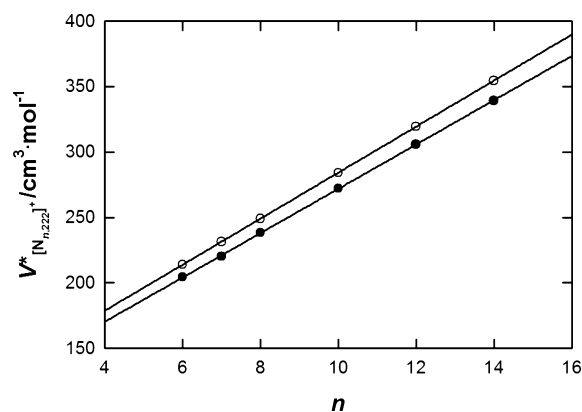
**Table 4. Effective Molar Volumes of Cations as Obtained from Equation 7 as Function of the Temperature at 0.1 MPa**

ion	Effective Molar Volumes/cm <sup>3</sup> ·mol <sup>-1</sup>			
	<i>M</i> g·mol <sup>-1</sup>	<i>C</i> <sub>0</sub> cm <sup>3</sup> ·mol <sup>-1</sup>	10 <sup>1</sup> · <i>C</i> <sub>1</sub> cm <sup>3</sup> ·mol <sup>-1</sup> ·K <sup>-1</sup>	10 <sup>5</sup> · <i>C</i> <sub>2</sub> cm <sup>3</sup> ·mol <sup>-1</sup> ·K <sup>-2</sup>
[Ntf <sub>2</sub> ] <sup>-13</sup>	280.15	157.597	1.043	5.052
[N <sub>6,222</sub> ] <sup>+</sup>	186.36	204.312	1.197	43.24
[N <sub>7,222</sub> ] <sup>+</sup>	200.38	220.266	1.517	29.52
[N <sub>8,222</sub> ] <sup>+</sup>	214.41	238.151	1.504	23.36
[N <sub>10,222</sub> ] <sup>+</sup>	242.46	272.096	1.800	6.549
[N <sub>12,222</sub> ] <sup>+</sup>	270.52	305.822	2.050	5.594
[N <sub>14,222</sub> ] <sup>+</sup>	298.57	339.126	2.286	10.15

From this work, an analysis of the [N<sub>*n*,222</sub>]<sup>+</sup> effective molar volumes as function of the alkyl chain at fixed temperature, was performed and, as expected based upon imidazolium based ILs, showed a linear trend with the alkyl chain at (298.15 and 363.15) K (see Figure 2).

A new relationship was finally calculated and expressed as a function of the reduced temperature using following eqs 8 to 9:

$$V_{[N_n,222]^+}^*(T^*) = V_{[N_0,222]^+}^*(T^*) + n\xi^*(T^*) \quad (8)$$



**Figure 2.** Effective molar volume of [N<sub>*n*,222</sub>]<sup>+</sup> as a function of alkyl chain length, *n*, for a series of [N<sub>*n*,222</sub>][Ntf<sub>2</sub>]<sup>-</sup> ILs at ●, 298.15 K and ○, 363.15 K.

where  $\xi^*$  is the contribution to the molar volume of a  $\text{CH}_2$  group on the alkyl chain and  $n$  is the number of  $-\text{CH}_2-$  groups in the alkyl chain on studied ammonium-based ILs. Using eq 7 and the effective molar volume of  $[\text{N}_{n,222}]^+$  cations calculated as a function of the temperature, the effective molar volume of the  $[\text{N}_{0,222}]^+$  and the contribution of a  $\text{CH}_2$  group in the alkyl chain as a function of temperature (parameters  $D_i$  and  $E_i$ ) have been calculated. Quadratic equations were found adequate for fitting the variation of these parameters with temperature.

$$V_{[\text{N}_{n,222}]^+}^*(T^*) = \sum_{i=0}^2 (D_i(T^*)^i) + n \left( \sum_{i=0}^2 (E_i(T^*)^i) \right) \quad (9)$$

Parameters  $D_i$  and  $E_i$ , determined from the  $[\text{N}_{n,222}]^+$  contribution and calculated effective molar volumes, are summarized in Table 5 within an absolute average relative

**Table 5. Parameters Associated with Equation 9 for the Prediction of Effective Molar Volumes of  $[\text{N}_{n,222}]^+$  Cations as a Function of Temperature from (293.15 to 363.15) K**

	$D_0$ $\text{cm}^3 \cdot \text{mol}^{-1}$	$10^2 \cdot D_1$ $\text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	$10^4 \cdot D_2$ $\text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-2}$
$[\text{N}_{0,222}]^+$	102.6	5.110	5.918
	$E_0$ $\text{cm}^3 \cdot \text{mol}^{-1}$	$10^2 \cdot E_1$ $\text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	$10^5 \cdot E_2$ $\text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-2}$
$\xi^*$	16.920	1.279	-4.153

deviation up to 0.09 %. The contribution to the molar volume of a  $\text{CH}_2$  group on the alkyl chain of the  $[\text{N}_{n,222}]^+$  is close to  $16.92 \text{ cm}^3 \cdot \text{mol}^{-1}$  at 298.15 K, a similar value as observed in the case of imidazolium-based ILs, for example,  $16.97 \text{ cm}^3 \cdot \text{mol}^{-1}$  at 298.15 K.<sup>13</sup> This observation allows the possibility to extend the present group contribution model initially proposed by Rebelo et al.<sup>15</sup> to a more sophisticated model.

**Coefficient of Thermal Expansion.** The evolution of the volumetric properties with temperature can be expressed by calculating the coefficient of thermal expansion  $\alpha_p$  defined as

$$\alpha_p = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p = -\frac{1}{\rho} \left( \frac{\partial \rho}{\partial T} \right)_p \quad (10)$$

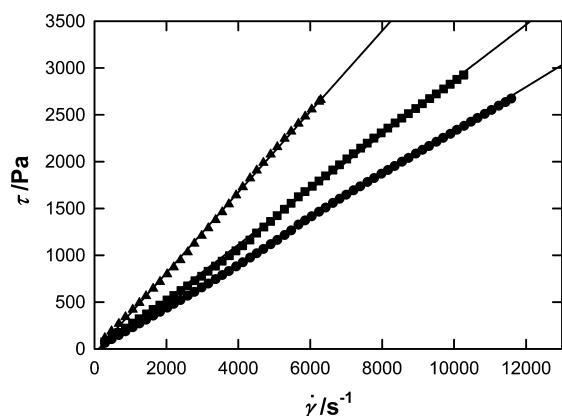
The values of  $\alpha_p$  for the dried samples calculated at (293.15 and 363.15) K from the fitted densities are presented in Table 6. Since the densities decrease linearly with temperature it is obvious that  $\alpha_p$  values are positive and increase with increasing temperature. The values obtained vary between  $(6.5 \text{ and } 7) \cdot 10^{-4} \text{ K}^{-1}$  in the case of studied samples. Values for  $\alpha_p$  of the same order of magnitude ( $5 \text{ to } 7) \cdot 10^{-4} \text{ K}^{-1}$  were reported in literature for several ILs containing  $[\text{Ntf}_2]^-$ ,  $[\text{BF}_4]^-$ , and  $[\text{PF}_6]^-$

**Table 6. Calculated Coefficients of the Thermal Expansion ( $\alpha_p/\text{K}^{-1}$ ) of Dried ILs at (293.15 and 363.15) K**

IL	$10^4 \cdot \alpha_p / \text{K}^{-1}$	
	293.15 K	363.15 K
$[\text{N}_{6,222}][\text{Ntf}_2]$	6.69	7.02
$[\text{N}_{7,222}][\text{Ntf}_2]$	6.99	7.35
$[\text{N}_{8,222}][\text{Ntf}_2]$	6.58	6.89
$[\text{N}_{10,222}][\text{Ntf}_2]$	6.49	6.80
$[\text{N}_{12,222}][\text{Ntf}_2]$	6.52	6.84
$[\text{N}_{14,222}][\text{Ntf}_2]$	6.59	6.91

anions and other ammonium, imidazolium, and pyridinium based cations.<sup>6,12,17,21</sup> The trends observed for the densities can be also noticed in the thermal expansion coefficients. From comparison of present data with literature values, it appears also that the imidazolium-based ILs exhibit a higher thermal expansion than the ammonium-based ones. The present results also suggest that the alkyl chain length does not affect strongly the thermal expansion coefficient in comparison to the anion effect on this property as already described in previous work.<sup>12,17,21</sup>

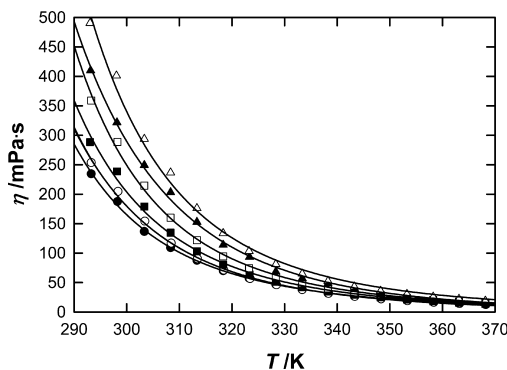
**Viscosity Measurements.** An example of flow behavior of the dried samples is shown in Figure 3. A similar trend is



**Figure 3.** Flow curves for selected  $[\text{NTf}_2]^-$  based ILs at 298.15 K. ●,  $[\text{N}_{6,222}][\text{Ntf}_2]$ ; ■,  $[\text{N}_{8,222}][\text{Ntf}_2]$ ; ▲,  $[\text{N}_{12,222}][\text{Ntf}_2]$ .

observed for each of the studied ILs. Linear relationships between shear stress,  $\tau$ , and shear rate,  $\dot{\gamma}$ , were obtained for selected ILs at 298.15 K and at 323.15 K. This linear relationship between the shear stress and the shear rate corresponds to a Newtonian behavior. This result is in agreement with the behavior described in literature for other bis{(trifluoromethyl)sulfonyl}imide-based ILs.<sup>1,3,16,17</sup>

The experimental viscosities of the dried samples from (293.15 to 368.15) K are shown in Figure 4 and summarized in Table 7. Furthermore, experimental viscosities of three water-saturated samples ( $[\text{N}_{6,222}][\text{Ntf}_2]$ ,  $[\text{N}_{8,222}][\text{Ntf}_2]$ , and  $[\text{N}_{12,222}][\text{Ntf}_2]$ ) from (293.15 to 323.15) K are listed in Table 8. Viscosity was not measured at higher temperatures for these



**Figure 4.** Experimental viscosities of the dried ILs as a function of temperature at 0.1 MPa. Effect of the cation alkyl chain length on the densities of  $[\text{Ntf}_2]^-$  based ILs: ●,  $[\text{N}_{6,222}]^+$ ; ○,  $[\text{N}_{7,222}]^+$ ; ■,  $[\text{N}_{8,222}]^+$ ; □,  $[\text{N}_{10,222}]^+$ ; ▲,  $[\text{N}_{12,222}]^+$ ; △,  $[\text{N}_{14,222}]^+$ . The lines correspond to the fit of the data by eq 11 reported in Table 9.

**Table 7. Experimental Viscosities ( $\eta$ ) of Dried ILs as a Function of Temperature at Atmospheric Pressure**

T/K	$\eta$ /mPa·s	T/K	$\eta$ /mPa·s	T/K	$\eta$ /mPa·s
[N <sub>6,222</sub> ][Ntf <sub>2</sub> ]		[N <sub>7,222</sub> ][Ntf <sub>2</sub> ]		[N <sub>8,222</sub> ][Ntf <sub>2</sub> ]	
293.25	234.5	293.25	253.6	293.05	288.4
298.25	187.5	298.35	204.6	298.15	238.7
303.35	136.7	303.45	154.2	303.35	178.9
308.35	109.2	308.45	116.9	308.35	134.7
313.35	87.67	313.45	90.36	313.35	103.1
318.35	69.87	318.45	71.04	318.35	80.41
323.25	57.54	323.45	56.80	323.35	63.70
328.35	46.72	328.45	46.10	328.35	51.16
333.35	38.13	333.35	37.89	333.25	41.95
338.25	31.82	338.35	31.52	338.25	34.75
343.25	26.73	343.35	26.37	343.35	29.24
348.35	22.80	348.35	22.26	348.25	24.75
353.25	19.60	353.35	19.05	353.25	21.10
358.25	16.86	358.35	16.41	358.25	18.11
363.15	14.62	363.25	14.33	363.15	15.62
368.15	12.78	368.25	12.68	368.15	13.60
[N <sub>10,222</sub> ][Ntf <sub>2</sub> ]		[N <sub>12,222</sub> ][Ntf <sub>2</sub> ]		[N <sub>14,222</sub> ][Ntf <sub>2</sub> ]	
293.25	358.9	293.15	410.0	293.05	490.3
298.25	288.6	298.15	321.6	298.05	401.1
303.35	214.5	303.35	249.2	303.35	293.6
308.35	160.1	308.35	203.1	308.35	236.5
313.35	122.0	313.35	152.7	313.35	176.1
318.35	94.47	318.35	113.9	318.35	133.6
323.25	74.37	323.35	93.33	323.25	103.2
328.35	59.72	328.35	68.19	328.35	81.04
333.35	48.60	333.35	56.88	333.35	64.89
338.25	40.11	338.25	48.28	338.25	52.42
343.25	33.52	343.35	38.65	343.25	43.08
348.35	28.36	348.25	31.43	348.25	35.84
353.25	24.11	353.25	28.35	353.25	30.16
358.25	20.40	358.25	23.00	358.25	25.63
363.15	17.56	363.15	19.38	363.15	22.01
368.15	15.21	368.15	17.24	368.15	18.99

samples since the results would be affected by the vaporization of water.<sup>17</sup> Kilaru and Scovazzo<sup>10</sup> give one single value of viscosity of [N<sub>6,222</sub>][Ntf<sub>2</sub>] at 303.15 K, and Sun et al.<sup>11</sup> measured the viscosity of [N<sub>6,222</sub>][Ntf<sub>2</sub>], [N<sub>7,222</sub>][Ntf<sub>2</sub>], and [N<sub>8,222</sub>][Ntf<sub>2</sub>] at 298.15 K. Data from both papers show different values of agreement ranging from (10 to 70) % in absolute value; their comparison with our results is therefore inconclusive.

The trends of the dependence of viscosity on cation and anion structure are in many aspects inverse to those observed

for density. In fact, it appears that viscosity increases with increasing alkyl chain length. Longer alkyl chain lengths in the [N<sub>n,222</sub>]<sup>+</sup> not only lead to heavier and bulkier cations but give rise to increasing van der Waals attractions between the aliphatic alkyl chains.<sup>3,17</sup> As shown by molecular simulation in the case of imidazolium-based ILs for alkyl chain length above butyl, and up to dodecyl,<sup>23</sup> the pure IL phase can be defined as a microstructured fluid by nonpolar and polar domains, which are formed by the alkyl chains and the charged parts, respectively. By using this model in the case of studied ammonium ions, the nitrogen, which corresponds to the polar domain, attached on the alkyl chain length has an electron-withdrawing effect on the three nearest CH<sub>2</sub> groups. The electron-withdrawing effect of the nitrogen on the alkyl chain length would decrease rapidly for further CH<sub>2</sub> groups. This part, almost free from the electron-withdrawing effect of the ionic headgroup of the cation, would be more susceptible to undergo van der Waals interactions, thus corresponding to an increase of viscosity for higher alkyl chain length.

The presence of water decreases strongly the viscosity of the sample: viscosity values at 293.15 K are (3.0, 2.7, and 2.6) times lower in the water-saturated sample as compared to the viscosity in the dried one, in the case of [N<sub>6,222</sub>][Ntf<sub>2</sub>], [N<sub>8,222</sub>][Ntf<sub>2</sub>], and [N<sub>12,222</sub>][Ntf<sub>2</sub>], respectively. Similar evolutions were observed for the study of the effect of water as a function of temperature on the viscosity for these three studied IL samples, within the difference of viscosities between the saturated sample and dried samples up to (2.2, 2.1, and 2.4) times, at 323.15 K, in the case of [N<sub>6,222</sub>][Ntf<sub>2</sub>], [N<sub>8,222</sub>][Ntf<sub>2</sub>], and [N<sub>12,222</sub>][Ntf<sub>2</sub>], respectively.

As illustrated in Figure 4 and shown in Tables 7 and 8, the viscosity drastically decreases with temperature in the studied temperature range. This is again the most striking for dried [N<sub>14,222</sub>][Ntf<sub>2</sub>], 26 times more viscous at 293 K than at 368 K. At 293 K, large differences in the data measured for the investigated ILs were observed. For example viscosities ranging from (230 to 490) mPa·s and from (80 to 158) mPa·s were observed for the dried and water-saturated samples, respectively. On the other hand, viscosity values tend to less significant differences at higher temperatures and range from (12 to 19) mPa·s at 368 K for the dried samples. Thus, it is obvious that as the viscosity decreases with increasing temperature the effect of the presence of water is much less important, as shown in Tables 7 and 8.

According to Seddon et al.,<sup>16</sup> ILs present generally a non-Arrhenius behavior, hence the Vogel–Tamman–Fülcher (VTF) equation is recommended to describe the variation of the transport properties as the function of temperature:

**Table 8. Experimental Viscosities ( $\eta$ ) of Water-Saturated ILs as a Function of Temperature at Atmospheric Pressure**

[N <sub>6,222</sub> ][Ntf <sub>2</sub> ] sat.			[N <sub>8,222</sub> ][Ntf <sub>2</sub> ] sat.			[N <sub>12,222</sub> ][Ntf <sub>2</sub> ] sat.		
T/K	$\eta$ /mPa·s	R <sup>a</sup>	T/K	$\eta$ /mPa·s	R	T/K	$\eta$ /mPa·s	R
293.25	79.28	3.0	293.25	107.8	2.7	293.25	157.4	2.6
298.05	66.69	2.8	298.05	88.06	2.7	298.05	130.7	2.5
303.05	53.98	2.5	303.05	69.84	2.6	302.95	97.24	2.6
308.05	44.04	2.5	318.05	55.76	2.4	308.05	76.56	2.7
313.05	36.49	2.4	313.05	45.09	2.3	313.05	60.67	2.5
318.05	30.73	2.3	318.05	36.51	2.2	318.05	48.79	2.3
322.95	25.98	2.2	323.05	29.74	2.1	322.95	39.19	2.4

$$^a R = (\eta_{\text{dried IL}} / \eta_{\text{water-saturated IL}}).$$

$$\eta = \eta_0 \exp\left(\frac{B}{T - T_0}\right) \quad (11)$$

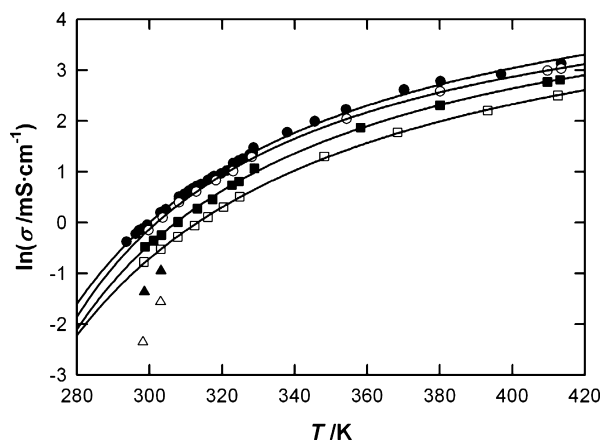
where  $B$ ,  $\eta_0$ , and  $T_0$  are adjustable parameters reported in Table 9.

**Table 9. Correlation Parameters of the VTF Equation (eq 11:  $\eta_0$ ,  $B$ , and  $T_0$ ) with the Deviations of the Fit  $SD_\eta^a$  for the Viscosity of Dried ILs as a Function of Temperature Determined from Measurements between (293 and 368) K**

IL	$10^3 \cdot \eta_0 / \text{mPa}\cdot\text{s}$	$B / \text{K}$	$T_0 / \text{K}$	$SD_\eta / \text{mPa}\cdot\text{s}$
$[\text{N}_{6,222}][\text{Ntf}_2]$	16.0	1653	121.1	2
$[\text{N}_{7,222}][\text{Ntf}_2]$	7.92	1880	112.5	3
$[\text{N}_{8,222}][\text{Ntf}_2]$	9.92	1837	114.5	6
$[\text{N}_{10,222}][\text{Ntf}_2]$	9.85	1825	119.4	7
$[\text{N}_{12,222}][\text{Ntf}_2]$	17.7	1745	119.5	8
$[\text{N}_{14,222}][\text{Ntf}_2]$	14.7	1833	117.6	$1 \cdot 10^4$

$^a SD_\eta = ((\sum (\eta_i^{\text{exp}} - \eta_i^{\text{cal}})^2) / (n - \nu))^{0.5}$  with  $n$  as the number of experimental points and  $\nu$  as the number of adjustable parameters.

**Conductivity Measurements.** As illustrated in Figure 5 and shown in Table 10, in the temperature range studied, the



**Figure 5.** Experimental conductivities of the dried ILs as a function of temperature at 0.1 MPa. Effect of the cation alkyl chain length on the densities of  $[\text{Ntf}_2]^-$  based ILs: ●,  $[\text{N}_{6,222}]^+$ ; ○,  $[\text{N}_{7,222}]^+$ ; ■,  $[\text{N}_{8,222}]^+$ ; □,  $[\text{N}_{10,222}]^+$ ; ▲,  $[\text{N}_{12,222}]^+$ ; △,  $[\text{N}_{14,222}]^+$ . The lines correspond to the fit of the data by eq 12 reported in Table 11.

conductivity increases with increasing temperature. As expected, the conductivity decreases with the number of carbon on the alkyl chain length of the cation, a contrario of the viscosity. In light of this observation, the mobility decreases with increasing of the van der Waals forces. For example, at 298.15 K the conductivity decreases up to 7 times by changing the alkyl chain length from  $n = 6$  to 14 on the ammonium  $[\text{N}_{n,222}]^+$  cation. Additionally, by increasing the temperature from (300 to 413.5) K, the conductivity increases up to around 24 times in the case of the  $[\text{N}_{6,222}][\text{Ntf}_2]$ .

Similarly to viscosity, the VTF equation may be used to describe the temperature dependence of conductivity of the measured ILs:

$$\sigma = \sigma_0 \exp\left(\frac{-B'}{T - T_0}\right) \quad (12)$$

**Table 10. Experimental Conductivities ( $\sigma$ ) of Dried ILs as a Function of Temperature at Atmospheric Pressure**

$T / \text{K}$	$\sigma / \text{mS}\cdot\text{cm}^{-1}$	$T / \text{K}$	$\sigma / \text{mS}\cdot\text{cm}^{-1}$	$T / \text{K}$	$\sigma / \text{mS}\cdot\text{cm}^{-1}$
$[\text{N}_{6,222}][\text{Ntf}_2]$		$[\text{N}_{6,222}][\text{Ntf}_2]$		$[\text{N}_{7,222}][\text{Ntf}_2]$	
293.65	0.685	323.05	3.220	299.75	0.860
296.15	0.798	324.55	3.360	303.65	1.100
297.15	0.857	325.65	3.510	308.15	1.480
298.15	0.887	327.65	3.820	312.85	1.840
299.35	0.953	328.35	3.880	318.25	2.280
302.95	1.213	328.45	3.950	323.05	2.750
304.45	1.292	328.65	4.350	328.15	3.620
308.15	1.597	337.95	5.900	354.35	7.720
308.15	1.663	345.55	7.320	380.05	13.22
309.65	1.754	354.15	9.280	409.65	19.88
310.85	1.865	370.15	13.60	413.45	20.64
311.85	1.944	380.15	16.14		
313.05	2.060	396.85	18.60		
314.15	2.120	413.45	22.84		
316.05	2.310				
317.15	2.410				
317.65	2.470				
317.95	2.480				
319.65	2.610				
321.25	2.780				
$[\text{N}_{8,222}][\text{Ntf}_2]$		$[\text{N}_{10,222}][\text{Ntf}_2]$		$[\text{N}_{12,222}][\text{Ntf}_2]$	
298.75	0.620	298.45	0.46	298.55	0.26
301.15	0.700	303.05	0.59	303.15	0.39
303.25	0.780	307.75	0.75		
313.15	1.310	316.05	1.11		
317.35	1.580	320.35	1.35	$[\text{N}_{14,222}][\text{Ntf}_2]$	
322.65	2.08	324.85	1.66	298.15	0.10
324.65	2.24	348.15	3.67	303.05	0.21
328.85	2.90	368.35	5.90		
358.15	6.49	393.18	9.03		
380.05	10.08	412.55	12.18		
409.65	15.87				
413.15	16.61				

where  $B'$ ,  $\sigma_0$ , and  $T_0$  are adjustable parameters summarized in Table 11.

**Table 11. Correlation Parameters of the VTF Equation (eq 12:  $\sigma_0$ ,  $B'$ , and  $T_0$ ) with the Deviations of the Fit  $SD_\sigma^a$  for the Conductivity of Dried ILs as a Function of Temperature Determined from Measurements between (293.15 and 413.15) K**

IL	$\sigma_0 / \text{mS}\cdot\text{cm}^{-1}$	$B' / \text{K}$	$T_0 / \text{K}$	$SD_\sigma / \text{mPa}\cdot\text{s}$
$[\text{N}_{6,222}][\text{Ntf}_2]$	348.05	542.57	207.21	0.57
$[\text{N}_{7,222}][\text{Ntf}_2]$	217.87	462.79	216.07	0.15
$[\text{N}_{8,222}][\text{Ntf}_2]$	224.95	528.90	209.64	0.10
$[\text{N}_{10,222}][\text{Ntf}_2]$	218.92	614.68	199.21	0.10

$^a SD_\sigma = ((\sum (\sigma_i^{\text{exp}} - \sigma_i^{\text{cal}})^2) / (n - \nu))^{0.5}$  with  $n$  as the number of experimental points and  $\nu$  as the number of adjustable parameters.

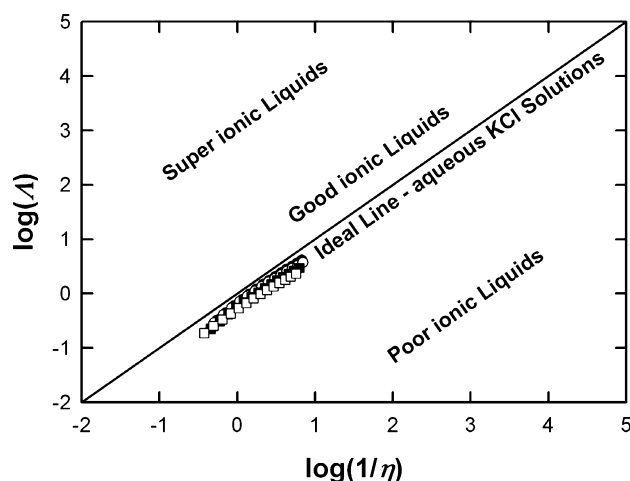
Values of conductivity at 298.1 K for  $[\text{N}_{6,222}][\text{Ntf}_2]$ ,  $[\text{N}_{7,222}][\text{Ntf}_2]$ , and  $[\text{N}_{8,222}][\text{Ntf}_2]$  were reported by Sun et al.,<sup>11</sup> but as in the case of density and viscosity values their comparison to data presented in this work is inconclusive as they were obtained at a single temperature. In other words, further investigations using other apparatuses and/or liquid batches could actually help quantify the agreement between



data reported in this work and literature values. A comparison of a larger number of data sets would contribute to this, since it is well-known that physical properties of ILs are very sensible to moisture, halide, and starting material contents.<sup>1,3,12–17,20</sup> When several extensive data sets are available, their description by a relevant thermodynamic model using a robust gnostic regression of the model parameters leads to valuable information of the distribution of the standard deviations of the data. “Good data” should present Gaussian deviation distributions; on the other hand, unreliable data, measured with different levels of uncertainty or by different people, often show several maxima on the distribution curve.<sup>7,8</sup> Obviously, due to the above-remarked scarcity of literature data of the ILs studied in this work, such a comparison could not be carried out. However, our statement is corroborated by a comparison of data in the National Institute of Standards and Technology (NIST) Ionic Liquids database,<sup>20</sup> from which it appears that volumetric and transport properties of ILs can differ up to (2 and 50) %, respectively. From there the necessity arose to develop and undertake rigorous thermodynamic studies, such as that carried out by the International Union of Pure and Applied Chemistry (IUPAC) in the case of the 1-hexyl-3-methyl-imidazolium bis{(trifluoromethyl)sulfonyl}imide.

**Ionicity.** A classical Walden rule diagram was used to determine the ionicity of studied ILs. From that the ionic mobilities were represented through the equivalent conductivity,  $\Lambda = V_m \cdot \sigma$  ( $S \cdot cm^2 \cdot mol^{-1}$ ), as function of fluidity (Poise<sup>-1</sup>),  $\phi = 1/\eta$ , of the medium, which is related to the ion mobility.<sup>24,25</sup>

Figure 6 shows the variation of  $\log(\Lambda)$  versus  $\log(1/\eta)$  at various temperatures from (298.15 to 363.15) K for selected



**Figure 6.** Walden plot showing the classification of investigated ILs: ●,  $[N_{6,222}][Ntf_2]$ ; ○,  $[N_{7,222}][Ntf_2]$ ; ■,  $[N_{8,222}][Ntf_2]$ ; □,  $[N_{10,222}][Ntf_2]$ . The line corresponds to the Walden Plot ideal line corresponding to aqueous KCl solution.<sup>24,25</sup>

ILs. According to the Walden rule, the ideal line represents fully dissociated ionic solutions having ions of equal mobility such as aqueous KCl solutions at high dilution.<sup>24,25</sup> The ionicity rule of studied ILs are presented and then compared with zones corresponding to individual types of electrolytes, as shown in Figure 6, as “good”, “poor”, and “superionic” ILs, respectively.<sup>26</sup> All studied ILs in this work conform to the Walden rule.

Furthermore, the ionicity of the studied ammonium-based ILs seems to be regrouped in a wide zone on the Walden plot, which corresponds to the “good” ILs zone of this

representation. From this figure, it appears also that the alkyl chain length on the ammonium cation does not affect the ionicity of involved ILs.

## CONCLUSIONS

In this paper a systematic study of thermophysical properties of a homologous series of *N*-alkyl-triethylammonium bis{(trifluoromethyl)sulfonyl}imide ILs is presented. Volumetric properties, rheologic properties, and ionic conductivity of pure ILs as a function of temperature were measured. Based on the rheological measurements, Newtonian and non-Arrhenius behavior were observed for studied ammonium-based ILs. From present experimental data, other crucial information was then obtained, for example, the effect of temperature and the alkyl chain length on involved properties. As expected, it appears from this work that the density and viscosity decrease with temperature as opposed to conductivity. Furthermore, by increasing the alkyl chain length the density and conductivity decrease, while the viscosity increases. These effects can be then related to the balance between van der Waals and electrostatic forces in involved ILs. An investigation of the ionicity of these ILs was then realized using the Walden plot, which shows that the studied ammonium salts can be classified as “good” ILs, as well as that the alkyl chain length on the ammonium cation does not affect their ionicity. Finally, from the density measurements, new effective molar volumes were then calculated by using the Jacquemin et al.<sup>12–14</sup> group contribution model. From which, an extension of this model was then proposed in the case of involved ammonium-based ILs within a relatively good accuracy close to 0.1 %.

## AUTHOR INFORMATION

### Corresponding Author

\*J.J.: e-mail: johan.jacquemin@qub.ac.uk, phone: +44 28 9097 4389. M.B.: e-mail: bendova@icpf.cas.cz, phone: +420 220 390 301.

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### Notes

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