

Viscosity of (C₂–C₁₄) 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ionic liquids in an extended temperature range

Mohammad Tariq^a, Pedro J. Carvalho^b, João A.P. Coutinho^{c,*}, Isabel M. Marrucho^a, José N. Canongia Lopes^{a,c}, Luís P.N. Rebelo^{a,*}

^a Instituto de Tecnologia Química e Biológica, UNL, Av. República, Apt. 127, 2780-901 Oeiras, Portugal¹

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

^c Centro de Química Estrutural, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

ARTICLE INFO

Article history:

Received 27 July 2010

Received in revised form 18 October 2010

Accepted 19 October 2010

Available online 30 October 2010

Keywords:

Ionic liquids

Viscosity

Stabinger viscosimeter

Rolling ball viscosimeter

Vogel–Fulcher–Tamman equation

ABSTRACT

Dynamic viscosities of several members of the 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide, [C_nmim][NTf₂], ionic liquids family, with the cation alkyl side-chain length varying from 2 to 14 carbon atoms, have been measured in the 278.15 K to 393.15 K temperature range using two different apparatuses. To the best of our knowledge, it is the first time that such an extensive assessment of viscosity – in terms of the number of compounds of a single ionic liquid homologous series, of the broad range of temperature covered, and the use of two different experimental techniques – is reported. The use of two different instruments, using different methodologies, provides information about the uncertainties in the measurement of viscosity of ionic liquids, including its dependence on the presence of traces of water and other impurities. An extensive critical analysis of the deviations between the data measured in this work and those reported in literature has been carried out.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Ionic liquids are a new class of salts with a melting point below 100 °C, so that they are liquid at or near room temperature. Due to their remarkable properties, like negligible vapor pressure [1], high thermal stability [2,3], non-flammability [4], wide electrochemical window [5], enhanced solvent quality [6], tunable nature [7] and, above all, easy recycling procedures [8], they are considered to be potential substitutes of many traditional organic solvents. Nonetheless, their high viscosity is one of the major drawbacks regarding their successful application, mainly when used as neat substances, in reaction and separation processes. In general, ILs exhibit viscosities two to three orders of magnitude higher than traditional organic solvents, leading to problems in mixing, stirring and pumping operations as well as in other mass transport phenomena [9]. Although they can easily dissolve a large range of compounds, the high viscosity of the solutions often stands as a hindrance factor for their further use [10]. Due to the strong tem-

perature dependence of the ionic liquids viscosity, an alternative strategy could be to work in the high temperature region where the viscosity is comparable to that of organic solvents or to use small amounts of water, which has a tremendous effect on the ILs viscosity even at low temperatures.

Although several articles are available in the literature concerning the viscosity of 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide, [C_nmim][NTf₂] ionic liquids [1–21], detailed and systematic studies containing the entire homologous series in a wide range of temperature are scarce. For example, Dzyuba and Bartsch [11] reported several thermophysical properties, including the viscosity, at 298.15 K for some [C_nmim][NTf₂] ionic liquids while Tokuda et al. [12] addressed in detail the transport behavior of this family of ionic liquids. However, both these articles report data only on ionic liquids containing either an even number of carbon atoms in the alkyl side-chain of the imidazolium cation (*n* = 2, 4, 6, 8, 10) or a single temperature. As a continuation of our previous work on the thermophysical property characterization of the [C_nmim][Ntf₂] family of ionic liquids [13], an extensive study on the viscosity of most members of this family (*n* = 2–14) in the temperature range of 278.15–393.15 K is here reported for the first time.

Viscosity is one of the properties of ionic liquids that is more sensitive to the presence of water and other impurities, viz. halides

* Corresponding authors.

E-mail addresses: jcoutinho@ua.pt (J.A.P. Coutinho), luis.rebelo@itqb.unl.pt (L.P.N. Rebelo).

¹ <http://www.itqb.unl.pt>.

Table 1

Experimental viscosities, η (mPa s), of 1-alkyl-3-methylimidazolium bistriflamide [C_nmim][Ntf₂] ionic liquids measured in this work with both the Stabinger and the rolling ball (AMVn) viscometers at different temperatures and comparison with available literature data.

η /(mPa s)				η /(mPa s)			
T (K)	Stabinger	AMVn	Literature	T (K)	Stabinger	AMVn	Literature
[C ₂ mim][Ntf ₂]				[C ₃ mim][Ntf ₂]			
278	76.049		75.7 [26]	278	122.17		
283	60.146	59.803	52 [27] 63.6 [12] 60.1 [26]	283	92.601		
288	48.468			288	71.782		
293	39.707	39.545	34 [26,28,29] 36 [27] 40.1 [9] ^a 38.8 [12] 38.6 [26]	293	56.782	56.402	53 [30]
298	33.001		32 [27] 36.5 [30] 28 [31] 34.29, 34.1 [17] ^{b,c} 32.6 [12] 25 [11]	298	45.748		
303	27.781		26 [32,27] 28.7 [9] ^d 27.3 [12] 27.1 [26]	303	37.43		
308	23.663			308	31.074		
313	20.367	20.488	19 [27] 21.1 [9] ^e 20.3 [12] 19.4 [26]	313	26.131	26.167	
318	17.693			318	22.229		
323	15.499		15 [27] 15.6 [17] 16.2 [9] ^f 15.5 [12] 14.9 [26]	323	19.106		
328	13.679			328	16.583		
333	12.158	12.416	12 [27] 12.7 [9] ^g 11.9 [12] 11.8 [26]	333	14.503	14.821	
338	10.873			338	12.786		
343	9.784		9 [27] 9.55 [17] 10.3 [9] ^h 9.5 [12]	343	11.353		
348	8.848			348	10.145		
353	8.041	8.036	7.7 [12]	353	9.1181	9.251	
358	7.340			358	8.2402		
				373		6.320	
[C ₄ mim][Ntf ₂]				[C ₅ mim][Ntf ₂]			
278	137.62		140.4 [16] ⁱ	278	164.73	179.720	
283	104.14		108.0 [12] 106.1 [16] ^j 84 [18] 103.58 [33]	283	123.09	133.334	
288	80.163		81.6 [16] ⁱ 69 [18] 79.76 [33]	288	93.651		
293	62.99	63.049	63.0 [12] 63.9 [16] ^j 52 [34,28] 59.8 [9] ^j 58 [18] 62.67 [33]	293	72.763	78.440	70 [16]
298	50.618		49.9 [12] 50.5 [30] 51 [16] ⁱ 50.2 [35] 69 [36] 47 [18] 44 [11] 50.17 [33]	298	57.806		50 [21]
303	41.122		40.0 [12] 40.6 [9] ^k 41.5 [16] ⁱ 41 [18]	303	46.383		

Table 1 (Continued)

$\eta/(\text{mPa}\cdot\text{s})$				$\eta/(\text{mPa}\cdot\text{s})$			
T (K)	Stabinger	AMVn	Literature	T (K)	Stabinger	AMVn	Literature
308	33.892		40.80 [33] 34 [18]	308	37.92		
313	28.279	28.632	33.67 [33] 27.5 [12] 28.5 [16] ⁱ 28.7 [9] ⁱ 29 [18] 28.15 [33]	313	31.428	33.940	
318	23.919		23.82 [33]	318	26.375		
323	20.449		20.0 [12] 20.5 [16] ^j 22 [18] 20.36 [33]	323	22.396		
328	17.665		17.58 [33]	328	19.198		
333	15.376	16.005	15.0 [12] 15.46 [16] ⁱ 16.2 [9] ^m 17 [18] 15.31 [33]	333	16.604	18.520	
338	13.497		13.44 [33]	338	14.48		
343	11.928		11.5 [12] 11.98 [16] ^j 14 [18] 11.89 [33]	343	12.729		
348	10.612		10.68 [16] ⁱ 10.58 [33]	348	11.267		
353	9.501	9.911	9.2 [12] 9.53 [16] ⁱ 9.6 [9] ⁿ 9.47 [33]	353	10.037	10.890	
358	8.5526		8.53 [33]	358	8.9958		
373		6.548	6.40 [33]	373		7.190	
393		4.785		393		5.150	
[C ₆ mim][Ntf ₂]				[C ₇ mim][Ntf ₂]			
278	212.3		207.6 [15]	278	235.00		
283	155.94		161.3 [12] 153.3 [15] 148 [27]	283	182.82		
288	117.29		115.8 [15]	288	136.42		
293	90.13	87.840	90.5 [12] 86 [27] 89.26, 89.54 [15] ^o 60.59 [37] 86, 90 [38] ^{p,q}	293	104.17		
298	70.614		69.7 [12] 71.0, 71.5 [17] ^{b,c} 68 [27] 70.29, 70.09 [15] ^o 80.1 [30] 59 [11] 68 [38] ^c 80.7 [39] 69.82 [40]	298	81.111		
303	56.298		55.7 [12] 55 [27] 56.11 [15] 57 [38] ^q 55.57 [39]	303	64.284		
308	45.606		51.6 [39]	308	51.751		
313	37.467	37.080	37.2 [12] 37 [27] 37.41 [15] 36.2, 37.7 [38] ^{p,q} 36.89 [40]	313	42.282		
318	31.187		34.2 [39] ^r	318	34.994		
323	26.254		25.8 [12] 24.9 [17] 26 [27] 26.25 [15] 25.79 [40]	323	29.302		
328	22.346		24.3 [39]	328	24.807		
333	19.203	19.290	18.8 [12] 19 [27] 19.22 [15] 18.6, 19.5 [38] ^{p,q}	333	21.203		

Table 1 (Continued)

$\eta/(\text{mPa s})$				$\eta/(\text{mPa s})$			
T (K)	Stabinger	AMVn	Literature	T (K)	Stabinger	AMVn	Literature
338	16.648		18.81 [40]	338	18.303		
343	14.549		17.9 [39]	343	15.919		
			14.1 [12,17]				
			14.58 [15]				
			15 [27]				
			14.9 [38] ^a				
			14.23 [40]				
348	12.809		13.7 [39] ^s	348	13.948		
353	11.354	11.480	10.8 [12]	353	12.307		
			11.38 [15]				
			11.0, 11.4 [38] ^{p,q}				
358	10.128		10.6 [39]	358	10.926		
373		7.460	7.463 [15]	363	9.7529		
393		5.280					
[C ₈ mim][Ntf ₂]				[C ₉ mim][Ntf ₂]			
278	297.03			278	348.2		
283	214.79		200.2 [12]	283	249.7		
288	159.11			288	183.88		
293	120.46		115.1 [12]	293	138.55		
			121.7 [41]				
298	93.053		90.0 [12]	298	106.41		
			92.5 [42]				
			95 [30]				
			74 [11]				
303	73.199		71.4 [12]	303	83.354		
			73.61 [41]				
308	58.53			308	66.198		
313	47.504		46.5 [12]	313	53.426		
			47.39 [41]				
318	39.086			318	43.762		
323	32.559		31.8 [12]	323	36.279		
			32.67 [41]				
328	27.431			328	30.429		
333	23.346		22.7 [12]	333	25.775		
			23.38 [41]				
338	20.057			338	22.119		
343	17.379		16.7 [12]	343	19.091		
			17.36 [41]				
348	15.179			348	16.614		
353	13.353		12.7 [12]	353	14.53		
			13.35 [41]				
358	11.825			358	12.823		
				363	11.401		
[C ₁₀ mim][Ntf ₂]				[C ₁₂ mim][Ntf ₂]			
278	403.2			283	384.51		
283	287.62	292.436		288	277.46		
288	210.53			293	205		
293	157.52	159.414	153.88 [41]	298	154.33		
			142 [43]				
298	120.18		108.2, 111.2 [17] ^{b,c}	303	118.68		
			120.2 [30]				
			90 [11]				
303	93.45		91.84 [41]	308	93.714		
			98.5 [43]				
308	73.917			313	74.488		
313	59.369	60.505	58.49 [41]	318	60.079		
			72.8 [43]				
318	48.363			323	49.107		
323	39.91		36.3 [17]	328	40.636		
			39.41 [41]				
			51.5 [43]				
328	33.323			333	34.008		
333	28.124	29.304	27.78 [41]	338	28.756		
338	23.971			343	24.546		
343	20.617		18.20 [17]	348	21.136		
			20.28 [41]				
348	17.88			353	18.352		
353	15.626	16.138	15.50 [41]	358	16.047		
358	13.753			363	14.125		
373		10.001					
393		6.800					

Table 1 (Continued)

$\eta/(\text{mPa s})$				$\eta/(\text{mPa s})$			
T (K)	Stabinger	AMVn	Literature	T (K)	Stabinger	AMVn	Literature
[C ₁₄ mim][Ntf ₂]							
313	98.043						
318	78.061						
323	63.095						
328	51.681						
333	42.827						
338	35.866						
343	30.355						
348	25.926						
353	22.332						
358	19.385						
363	16.951						

^a T = 293.39 K.

^b Measured using Oscillating-piston viscometer.

^c Measured with a Cone-and-plate viscometer.

^d T = 303.48 K.

^e T = 313.03 K.

^f T = 322.59 K.

^g T = 332.12 K.

^h T = 341.45 K.

ⁱ Average values measured with a falling body viscometer, either of two different measurements with same sinker or of two different sinkers of 6.0 mm and 6.3 mm diameters.

^j T = 293.40 K.

^k T = 302.93 K.

^l T = 312.45 K.

^m T = 331.12 K.

ⁿ T = 350.47 K.

^o Values from two different runs for same sample with a Stabinger viscosimeter.

^p Sample containing water content in mass fraction between 58 and 562 ppm.

^q Sample containing water content in mass fraction between 10 and 160 ppm.

^r T = 318.05 K.

^s T = 348.05 K.

[14]. However, reported viscosity data often do not state either the water content or the samples purity. Only a handful of studies [9,15–18], describe the preparation of the samples, in particular drying, sample handling and purity checking, prior to the viscosity measurements. Therefore, the main objective of this work is two folded: (i) to perform a systematic study of the viscosity along this series of homologous ionic liquids in an extended range of temperature and (ii) to do a critical analysis of the viscosity data available in the literature. Adopting an approach previously used by Widegren and Magee [15] and Ahosseini et al. [17], two different methodologies (Stabinger and Rolling Ball viscosimeters) were used in order not only to validate the results but also to investigate the uncertainties related to the use of different experimental techniques for viscosity measurements. Furthermore, different correlation and prediction methods currently used for the estimation of the viscosity of pure ionic liquids were also evaluated. A large amount of auxiliary thermodynamic data (vapor pressure [2], enthalpy of vaporization [19], force field parameters [20] and both empirical [21,22] or simulation-based [23] correlations) are available for the [C_nmim][Ntf₂] family, highlighting again the obvious choice of this family of ionic liquids.

2. Experimental

2.1. Chemicals

The ionic liquids of the [C_nmim][NTf₂] family with $n=2, 3$ and 6 were synthesized and purified at Queen's University ionic liquid laboratory, Belfast. All other ionic liquids were purchased from Iolitec with a stated purity of 99%. NMR analysis shows no major impurities except traces of water. Before any measurements all samples were dried for at least 48 h under vacuum (0.1 Pa) and moderate temperature (beginning at room temperature and increasing gradually up to 333 K over a period of 6 h). The water

content of all samples was checked using a Karl–Fischer automated titration apparatus and found to be less than 70 ppm, much lower than the original values which were in the range of 2000–3000 ppm. The chloride content, determined using a chloride-specific electrode, was less than 20 ppm, an adequate value for this work.

2.2. Viscosity measurements

The viscosities were measured using either an Anton Paar AMVn micro viscometer or an automated SVM 3000 Anton Paar rotational Stabinger viscometer–densimeter.

The Anton Paar AMVn micro viscometer is based on the concept of a falling sphere inside a capillary of known diameter. Two laser sensors at the two ends of the capillary detect the small metal sphere and allow the determination of the time elapsed during its fall between the two positions. An average time is automatically recorded for the desired number of successive runs (11 in our case). The apparatus can be operated in a wide range of temperatures and angles. The temperature of the capillary is controlled by a Peltier device within a precision of ± 0.01 K. The average time for the different angles has been used to calculate the kinematic viscosity of each compound. The densities required for calculating the corresponding dynamical viscosities were taken from a previous work [13]. The measurements were made in two different capillaries of nominal diameter 3.0 and 1.6 mm for most of the ionic liquids. Since the viscosity of ionic liquids decreases considerably with temperature – and the corresponding falling times become very small (less than 10 s) – thinner tubes were used in order to minimize the errors in the measurements. To validate the results, the viscosity of each sample was measured at at least two selected angles. The overall uncertainty in the measurements was estimated to be of 2%.

Measurements of viscosity were also performed in the temperature range of 278 K to 363 K at atmospheric pressure using an automated SVM 3000 Anton Paar rotational Stabinger

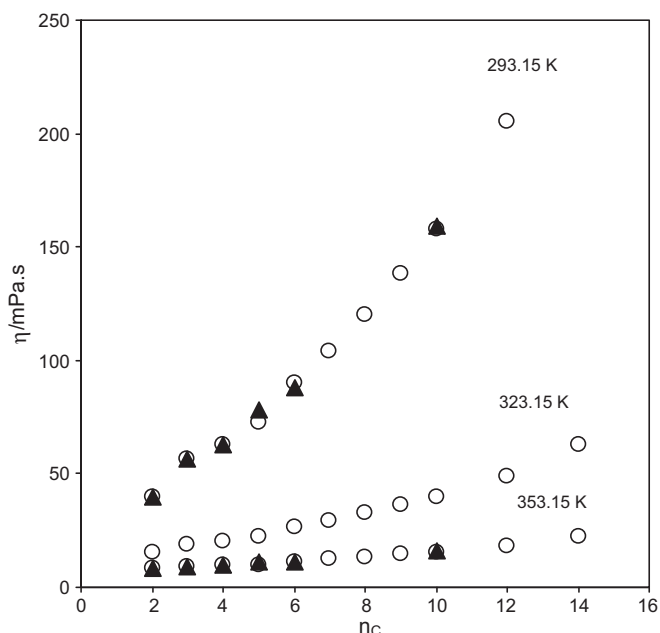


Fig. 1. Effect of alkyl chain length in the viscosity of $[C_n\text{mim}][\text{Ntf}_2]$ ionic liquids at different temperatures measured using the rolling-ball viscometer (▲) and the Stabinger viscometer (○).

viscometer–densimeter. These viscosity measurements are based on a tube filled with the sample in which floats a hollow measuring rotor. Due to its low density, the rotor is centered in the heavier liquid by buoyancy forces. The rotor is forced to rotate by shear stresses in the liquid and is guided axially by a built-in permanent magnet, which interacts with a soft iron ring. The rotating magnetic field delivers the speed signal and induces eddy currents in the surrounding copper casing. These eddy currents are proportional to the speed of the rotor and exert a retarding torque on the rotor. Two different torques influence the speed of the measuring rotor. At equilibrium, the two torques are equal and the viscosity can be traced back to a single speed measurement. The SVM 3000 uses Peltier elements for fast and efficient thermal stability. The temperature uncertainty is $\pm 0.02\text{ K}$ from 288.15 to 378.15 K. The precision of the dynamic viscosity measurements is $\pm 0.5\%$. The overall uncertainty of the measurements (taking into account the purity and handling of the samples) is estimated to be 2%. Further details about the equipment and method can be found elsewhere [24,25].

3. Results and discussion

The values of viscosities measured at different temperatures for all $[C_n\text{mim}][\text{Ntf}_2]$ ionic liquids using the two methodologies are presented in Table 1. For comparison purposes, reported literature values are also included in Table 1. A thorough analysis concerning the differences between our values and those reported in the literature is also presented in the following paragraphs. Viscosities measured by both methods used in this study (Stabinger and Rolling Ball) are in very good agreement with each other, irrespectively of the temperature, as depicted in Fig. 1.

From Fig. 1 it is clear that the viscosity of the ionic liquids increases monotonically, though not linearly, with the increase of the alkyl side-chain length of the cation. Some authors [11,12,34,30] also witnessed this behavior and have forwarded several explanations: (i) Bonhote et al. [34] proposed that this increase in viscosity is due to the increase of van der Waals interactions between alkyl side-chains of the cations in the homologous series;

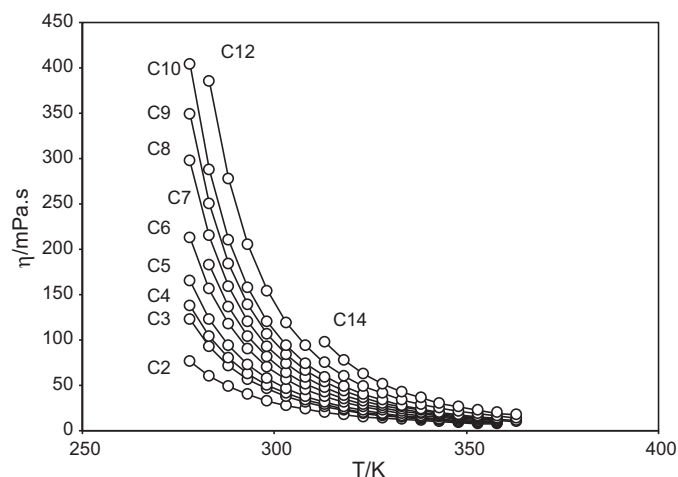


Fig. 2. Viscosity temperature dependence for $[C_n\text{mim}][\text{Ntf}_2]$ ionic liquids. Symbols represent experimental data. Solid lines are VFT (Eq. (1)) fits.

(ii) in the same line of thought, Tokuda et al. [12] suggested the use of the term “ionicity” to explain this type of behavior. Ionicity is defined by these authors as the proportion of ions (charged species) that contribute to the ionic conduction from the overall diffusing species. The use of the Walden rule enables the establishment of a direct relationship between ionicity and viscosity. These authors show that an increase of the alkyl side-chain length of the cation decreases the ionicity and this fact is explained again by an increase of van der Waals interactions between the alkyl side-chains of the cations; (iii) simulations studies [44] from our group have shown that imidazolium-based ionic liquids with alkyl chain length higher than $[C_6\text{mim}]^+$ exhibit the formation of nanostructural domains permeated by charged/polar network. This fact has been later supported by experimental evidence [45]. For short chain ILs the formation of nano-domains is not possible as the non-polar part is not large enough. The formation of such nano-segregated domains can also contribute to enhanced viscosity.

As can be seen in Fig. 2, the temperature has a profound effect on viscosity, i.e., the viscosity decreases exponentially with increasing temperature. However, at high temperatures, the viscosity values for all the ILs studied are all very close to each other in magnitude. For instance at 358 K, the viscosity of $[C_2\text{mim}][\text{Ntf}_2]$ is 7.3 mPa s whereas at same temperature the value of viscosity for $[C_{14}\text{mim}][\text{Ntf}_2]$ is 19.4 mPa s. This is a surprising fact giving the huge difference of 12- CH_2 groups in the alkyl chain length. The viscosity data measured in this work using the Stabinger viscometer were fitted using Vogel–Fulcher–Tamman (VFT) Eq. (1),

$$\eta = A \times e^{B/(T-T_g)} \quad (1)$$

where A and B are fitting parameters and T_g is the glass transition temperature. T_g is considered as a third fitting parameter, due to the unavailability or large dispersion in the reported T_g values for these ionic liquids. Table 2 shows all the fitting coefficients including the experimentally determined glass transition temperatures for these ionic liquids. The overall deviations between the smoothed values and raw data have also been reported for each IL in Table 2. It can be concluded that VFT satisfactory fits the data. It is also evident from Table 2 that the glass transition temperatures estimated using VFT equation (all between 157.4 and 167.2 K) and those experimentally determined (all between 181.2 and 192.4 K) are in a close range. However, the calculated values are always $\sim 20\text{ K}$ smaller than the experimental values.

Although the observed trends in terms of temperature and cation alkyl side-chain length have already been reported in the literature [11,12], there is a lot of ambiguity in the reported

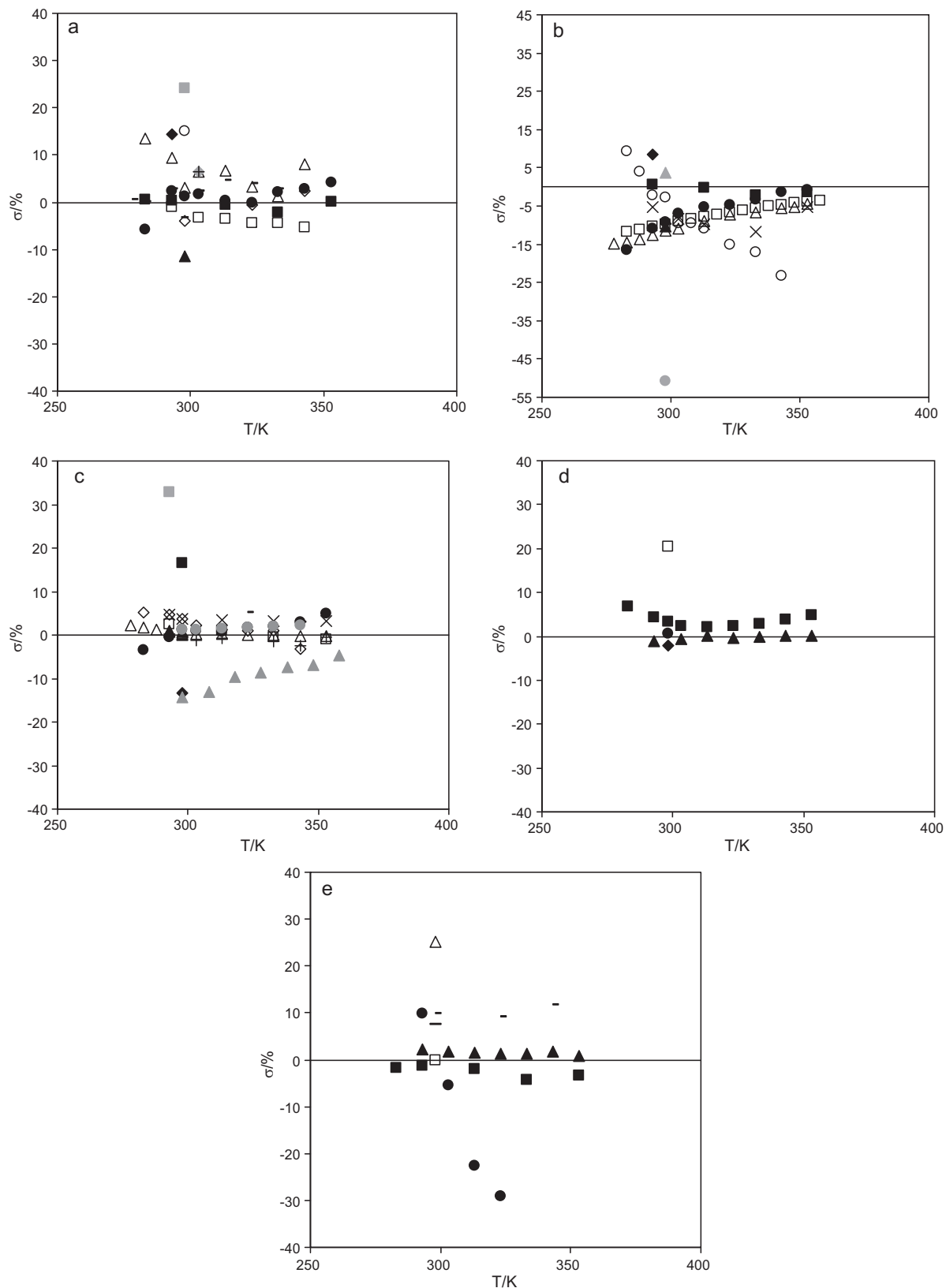


Fig. 3. Deviation ($100(\eta_{exp} - \eta_{lit})/\eta_{exp}$) of the literature viscosities from the data measured in this work for (a) $[C_2mim][Ntf_2]$: (■) AMVn, (Δ) Crosthwaite [27], (●) Tokuda [12], (◆) Bonhote [34], (\square) Jacquemin [9], (\blacktriangle) McHale [30], (o) McEwen [31], (\diamond) Ahosseini A [17], (—) Ahosseini B [17], (\diamond) Morgan [32], (+) Almantariotis [41], (—) Froba [26], (\square) Dzyuba [11]; (b) $[C_4mim][Ntf_2]$: (■) AMVn, (Δ) Harris [16], (●) Tokuda [12], (◆) Bonhote [34], (\times) Jacquemin [9], (\blacktriangle) McHale [30], (—) Kitaoka [35], (o) Huddlestone [36], (o) Okoturo [18], (Δ) Dzyuba [11], (\square) Tariq [33]; (c) $[C_6mim][Ntf_2]$: (\square) AMVn, (Δ) Widegren A [15], (●) Tokuda [12], (\diamond) Crosthwaite [27], (\blacktriangle) Widegren B [15], (\square) Ignatev [37], (—) Ahosseini A [17], (—) Ahosseini B [17], (◆) McHale [30], (■) Dzyuba [11], (\times) Kandil A [38], (+) Kandil B [38], (Δ) Marsh [39], (o) Santos [40]; (d) $[C_8mim][Ntf_2]$: (■) Tokuda [33], (\blacktriangle) Almantariotis [41], (●) Andreatta [42], (◆) McHale [30], (\square) Dzyuba [11]; and (e) $[C_{10}mim][Ntf_2]$: (■) AMVn, (\blacktriangle) Dmitri [41], (●) Gan [43], (—) Ahosseini A [17], (—) Ahosseini B [17], (\square) McHale [30].

Table 2

Fitting coefficients of VFT equation for the viscosity of the studied ionic liquids using the Stabinger apparatus and respective deviations between fitted and experimental values. The glass transition temperatures obtained in this work from VFT equation are compared with those from literature.

Ionic liquid	A	B	T_g (K)	$T_{g, \text{exp}}^a$ (K)	Deviation (σ) ^b
[C ₂ mim][Ntf ₂]	0.2281	692.5	158.9	181.15	0.0043
[C ₃ mim][Ntf ₂]	0.1966	713.7	167.2	186.15	0.0020
[C ₄ mim][Ntf ₂]	0.1488	794.7	161.8	184.51	0.0005
[C ₅ mim][Ntf ₂]	0.1263	838.2	161.3	187.88	0.0049
[C ₆ mim][Ntf ₂]	0.1254	855.9	163.0	189.83	0.0068
[C ₇ mim][Ntf ₂]	0.1168	888.1	162.4	187.95	0.0039
[C ₈ mim][Ntf ₂]	0.09972	943.3	160.2	188.37	0.0108
[C ₉ mim][Ntf ₂]	0.09534	971.0	159.8	188.64	0.0030
[C ₁₀ mim][Ntf ₂]	0.08095	1028.0	157.4	192.36	0.0094
[C ₁₂ mim][Ntf ₂]	0.08497	1040.0	159.6	–	0.0042
[C ₁₄ mim][Ntf ₂]	0.09854	1012.0	166.5	–	0.0061

^a Unpublished results from our group.

^b $\sigma = \left(\frac{\sum (\eta_i^{\text{exp}} - \eta_i^{\text{cal}})^2 / \eta_i^{\text{cal}}}{n-v} \right)^{0.5}$ where n is the number of experimental points, v the number of adjustable parameters.

viscosity data. To our knowledge, viscosity data has been extensively reported for [C₂mim][Ntf₂], [C₄mim][Ntf₂], [C₆mim][Ntf₂], [C₈mim][Ntf₂] and [C₁₀mim][Ntf₂] but only few data points have been reported for [C₃mim][Ntf₂] and [C₅mim][Ntf₂] only at a few temperatures (Table 1). The relative deviations between our viscosity values and those from different authors are presented in Fig. 3a–e for selected members of the family under study. The deviations between the viscosity values measured in this work and those predicted by the Orrick–Erbar and Gardas methods are listed in Table 3.

More than 10 authors reported [C₂mim][Ntf₂] viscosity values and there are large differences between our values and those previously reported (Fig. 3a), especially at low temperatures. This fact can be due to the presence of impurities, such as water and halides, in the samples but also related to experimental problems of temperature control, as indicated by Jacquemin et al. [9]. For instance, for [C₂mim][Ntf₂] at 298.15 K we measured a viscosity value of 60 mPa·s, whereas Crosthwaite et al. [27] reported 52 mPa·s – a difference of 13%. At intermediate temperatures the relative difference between these two data sets falls to 1% but then increases again in the high temperature region. A similar trend is also exhibited by the values reported by Tokuda et al. [12]. In general, in the low temperature region viscosity deviations can be as high as 24% [11] and as low as –11% [30]. To be mentioned that the viscosity values obtained in this work using the two different apparatuses are in excellent agreement with each other showing a maximum difference of ±2%.

Table 3

Average percentage deviations between the experimental and the predicted values of viscosities for all the studied ionic liquids. Data from different experimental methods was used.

Ionic liquid	$\delta\eta = \sum \{(\eta_{\text{exp}} - \eta_{\text{cal}}) \times 100 / \eta_{\text{exp}}\} / n$	
	Orrick–Erbar	Gardas
[C ₂ mim][Ntf ₂]	2.41	18.61
[C ₃ mim][Ntf ₂]	9.81	22.75
[C ₄ mim][Ntf ₂]	1.26	12.74
[C ₅ mim][Ntf ₂]	–5.52	4.04
[C ₆ mim][Ntf ₂]	–5.32	1.57
[C ₇ mim][Ntf ₂]	–10.80	–7.28
[C ₈ mim][Ntf ₂]	–17.95	–16.06
[C ₉ mim][Ntf ₂]	–22.95	–25.89
[C ₁₀ mim][Ntf ₂]	–34.95	–39.07
[C ₁₂ mim][Ntf ₂]	–50.40	–63.33
[C ₁₄ mim][Ntf ₂]	–37.24	–70.33

As for [C₄mim][Ntf₂], the deviation trends are similar to those found for [C₂mim][Ntf₂]. The differences at low temperatures between Harris et al. [16] and Tariq et al. [33] with our values are as high as –15%, although they reduce to –4% at high temperatures (Fig. 3b). Also, the data of Tokuda et al. [12] shows a difference of –16% at low temperatures and then merges to our data with just a small difference of –1% for temperatures higher than 300 K. Okoturo et al. [18] data exhibit a difference of 9% at low temperatures, agrees with our data at intermediate temperatures and deviates again for the high temperature region, showing a maximum deviation of –23%. Again, an excellent agreement is observed between the values of Stabinger and AMVn viscosimeters with only a maximum difference of ±2%. The most important point to emphasize here is that the [C₄mim][Ntf₂] samples used in this work were purchased from Iolitec, whereas the ionic liquid used in the viscosity measurements reported in Refs. [16,33] (those showing high deviations relative to the present data) were synthesized and purified in-house. ¹H NMR of our sample (Supporting Information) revealed impurity traces – probably starting materials – even after evacuating the samples under moderate temperatures for 48 h with vigorous stirring. On the other hand, the in-house sample used by us [33], after undergoing similar purification procedures, exhibited impurity levels below the detection limits of the NMR spectrometer. These facts lead to the conclusion that presence of impurities is probably one of the main causes of the large discrepancies found between viscosity values reported in the literature and thus special care has to be taken in reporting the properties of a commercial sample.

The majority of the reported viscosity results for [C₆mim][Ntf₂] presents small deviations from our data (Fig. 3c). Few exceptions are Ignatev et al. [37], who reported a viscosity value with a difference of 33%, while McEwen [31] and Dzyuba and Bartsch [11] reported results with a difference of –13% and 16%, respectively. The remaining viscosity data are in excellent agreement with the reported literature data showing deviations between ±1 and ±5% over the whole temperature range. This increasing accuracy for the larger members of the series can possibly be attributed to the smaller amount of water present when compared to the other members of the family with smaller alkyl chain lengths. The increase of the cation alkyl chain length, leads to an increase in the hydrophobicity of the IL and thereby, a small amount of water in the samples. It must be stressed that this particular ionic liquid was the object of an IUPAC-sponsored study where high-purity samples of a single batch of [C₆mim][Ntf₂] were distributed to different laboratories around the world that measured different types of thermophysical properties. The data were then compared in subsequent publications either by the individual groups or the IUPAC-led team. In the case of the viscosity measurements they were performed by four groups [15,38–40] using various methods. Widegren and Magee [15] used Stabinger and Ubbelohde viscometers to measure the viscosities with an expanded uncertainty of 2% and 5% in the high and low temperature regions, respectively. Kandil and Marsh [38] used a vibrating wire viscometer to measure the viscosity of two samples containing different water contents, with an expanded uncertainty of 2%. Comparing with our data, the sample with lowest water content displayed small deviations (0.1–0.4%) while the sample with highest water content showed higher deviations (3–4%). Seddon and collaborators in a contribution to the same IUPAC report [39] used a Cone-plate viscometer to measure viscosities of a similar sample and reported values that show deviations as high as 15% at low temperatures, which decrease to nearly 5% at high temperatures, when compared to the results presented in this work. Since, the water content is within the values usually found for this IL, these large deviations can be due to poor temperature control. Santos et al. [40] reported the measurements of similar sample using Ostwald viscometer. The

Table 4
Detailed summary of the water and halide contents as well as the methodology reported in literature for the $[C_n\text{mim}][\text{Ntf}_2]$ ionic liquid samples with $n=2, 4, 6, 8, 10$ (where, CP = Cone-plate, MV = Microviscometer, RH = Rheometer, OP = Oscillating Piston, SLS = Surface Light Scattering, OV = Ostwald Viscometer, FB = Falling Body, RB = Rolling Ball, ST = Stabinger, VW = Vibrating Wire and UB = Ubbelohde Viscometer).

Water content (ppm)	Halide content (ppm)	T_{range} (K)	η_{range} (mPa s)	Method	Reference
$[C_2\text{mim}][\text{Ntf}_2]$					
204	10	283–343	52–9	CP	Crosthwaite et al. [27]
40	–	283–353	63.6–7.7	CP	Tokuda et al. [12]
18–36	~0	293	34	MV	Bonhote et al. [34]
152	50	293–343	40.1–10.3	RH	Jacquemin et al. [9]
152	5	298	36.8	CP	McHale et al. [30]
24	36 (Br)	298–343	34.29–9.55	OP	Ahosseini et al. [17]
24	36 (Br)	298	34.1	CP	Ahosseini et al. [17]
509	–	278–333	75.7–11.8	SLS	Froba et al. [26]
–	–	298	25	OV	Dzyuba et al. [11]
–	–	298	28	–	McEwen et al. [31]
$[C_4\text{mim}][\text{Ntf}_2]$					
27	~0	278–353	140.4–9.53	FB	Harris et al. [16]
40	–	283–353	108–9.2	CP	Tokuda et al. [12]
18–36	~0	293	52	MV	Bonhote et al. [34]
143	50	293–353	59.8–9.6	RH	Jacquemin et al. [9]
138	5	298	50.5	CP	McHale et al. [30]
1719	–	298	50.2	CP	Kitaoka et al. [35]
474	–	298	69	CP	Huddleston et al. [36]
–	–	283–343	84–14	RB	Okoturo et al. [18]
–	–	298	44	OV	Dzyuba et al. [11]
70	–	283–373	71.49–6.40	ST	Tariq et al. [33]
$[C_6\text{mim}][\text{Ntf}_2]$					
14	~0	278–373	207.6–7.463	ST	Widegren et al. [15]
40	–	283–353	161.3–10.8	CP	Tokuda et al. [12]
31	10	283–343	148–15	CP	Crosthwaite et al. [27]
–	–	293	60.59	ST	Ignatev et al. [37]
125	8 (Br)	298–343	71–14.1	OP	Ahosseini et al. [17]
125	8 (Br)	298	71.5	CP	Ahosseini et al. [17]
18	5	298	80.1	CP	McHale et al. [30]
–	–	298	59	OV	Dzyuba et al. [11]
58–562	–	293–353	86–11	VW	Kandil et al. [38]
10–160	–	293–353	90–11.4	VW	Kandil et al. [38]
163–269	–	298–368	80.7–8.33	CP	Marsh et al. [39]
<200	–	298–343	69.82–14.23	OV	Santos et al. [40]
$[C_8\text{mim}][\text{Ntf}_2]$					
40	–	283–353	200.2–12.7	CP	Tokuda et al. [12]
110	5	293–353	121.7–13.35	RB	Almantariotis et al. [41]
48	19	298	92.51	UB	Andreatta et al. [42]
42	5	298	95	CP	McHale et al. [30]
–	–	298	74	OV	Dzyuba et al. [11]
$[C_{10}\text{mim}][\text{Ntf}_2]$					
115	5	293–353	153.88–15.5	RB	Almantariotis et al. [41]
–	–	293–323	142–51.5	CP	Gan et al. [43]
123	53 (Br)	298–343	108.2–18.2	OP	Ahosseini et al. [17]
123	53 (Br)	298	111.2	CP	Ahosseini et al. [17]
66	5	298	120.2	CP	McHale et al. [30]
–	–	298	90	OV	Dzyuba et al. [11]

reported water content was always less than 200 ppm. These values are in excellent agreement with our results, showing deviations of 1–2%.

As mentioned before the amount of viscosity data for $[C_8\text{mim}][\text{Ntf}_2]$ available in the literature is much scarce than for the previous members of the family. A difference of 8% was observed from the values reported by Tokuda et al. [12] at low temperatures which reaches a minimum (2%) around 313 K and then increases again to 5% for the high temperature region (Fig. 3d). Again, the viscosity data measured by Dzyuba and Bartsch [11] at 298.15 K (74 mPa s) shows a large difference (24%) from our values. All other reported viscosity data are in excellent agreement, showing deviations between 2% and 0.02%.

A large dispersion was observed for $[C_{10}\text{mim}][\text{Ntf}_2]$ between the literature data and those measured in this study (Fig. 3e). Since $[C_{10}\text{mim}][\text{Ntf}_2]$ is not very hygroscopic this may be attributed to purity issues of the ionic liquid itself, which can be especially important for heavy ILs. The values reported by Ahosseini et al. [17] are

consistently 10% higher than our data at all temperatures, while those from Gan et al. [43] show a difference of 10% at 293 K and reach deviations as high as –30% at 323 K. The data from Dzyuba and Bartsch [11] display a difference of 25% at 298.15 K. The values reported by Almantariotis et al. [41] and those measured in this work using the AMVn micro viscosimeter are in very good agreement, with deviations between 1 and 4%.

In an attempt to establish a clearer picture of the effect of the various experimental factors on the viscosity measurements, Table 4 presents a summary of all the experimental conditions reported in literature including the method used, water contents, halide (if given) and the range of temperature studied. All the authors used in house made samples. The first conclusion is that when there is no information on the purity, water content and methodology, as in case of Dzyuba and Bartsch [11], high deviations are always obtained. Also, as stated before, large deviations in the low and high temperature regions and small deviations at room temperature, as in the case of Tokuda et al. [12] data, is an indication of poor

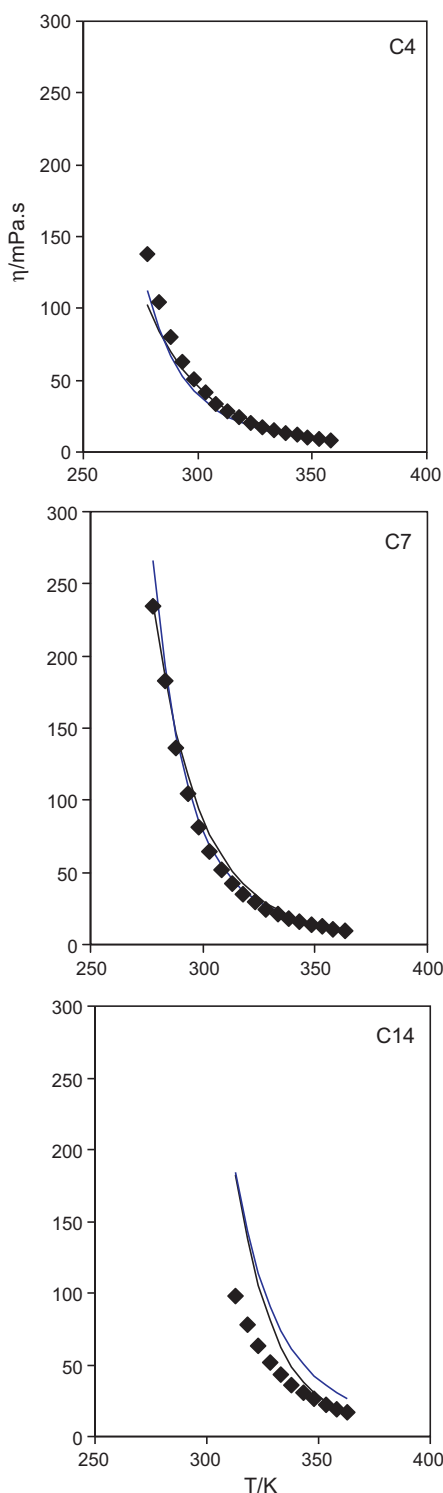


Fig. 4. Comparison between the viscosity data measured in this work (symbols) and those predicted by the Erick–Orber approach (solid line) and the Gardas and Coutinho method (dashed line) for $[C_4\text{mim}][\text{Ntf}_2]$, $[C_7\text{mim}][\text{Ntf}_2]$ and $[C_{14}\text{mim}][\text{Ntf}_2]$.

temperature control. Nevertheless, it is quite difficult to establish a cause/effect from the analysis of Table 4. For example, the viscosity data from Crosthwaite et al. [27] shows high positive deviations for $[C_2\text{mim}][\text{Ntf}_2]$ but very good agreement is obtained with the literature for $[C_6\text{mim}][\text{Ntf}_2]$. The water content in $[C_2\text{mim}][\text{Ntf}_2]$ is 204 ppm while in case of $[C_6\text{mim}][\text{Ntf}_2]$ it is only 31 ppm. If we consider that the high water content is responsible for large devi-

ations, the deviations in case of $[C_2\text{mim}][\text{Ntf}_2]$ should decrease at high temperatures, which is not the case. Thus, the cause of these deviations cannot be clearly established from Table 4.

3.1. Viscosity prediction

The large amount of data gathered in this study is also very valuable to test the performance of models, especially predictive models. Several methods are available in the literature to predict the viscosity of pure liquids based on group contribution methods [46], corresponding state principles [47] and simulations [23]. The viscosity experimental results obtained in this work were compared with predicted viscosities using two group-contribution methods.

The first method is a recently proposed group-contribution method [48] based on the Orrick–Erbar approach [46], which estimates the viscosity by fitting the A and B parameters of the following equation to viscosity data,

$$\ln\left(\frac{\eta}{\rho M}\right) = \frac{A+B}{T} \quad (2)$$

where η and ρ are the viscosity and density in $\text{mPa}\cdot\text{s}$ and $\text{g}\cdot\text{cm}^{-3}$, respectively. M is the molecular weight, and T is the absolute temperature in K. Instead of using this equation in a correlative sense, the values of parameters A and B can also be obtained from group contribution methods and are available in the literature [48]. In this way, Eq. (2) can also be used as a viscosity predictive tool, when the density of the ionic liquid under study is known.

Since the Arrhenius-type of viscosity dependence with temperature described by Eq. (2) is not completely adequate for ionic liquids, the second method used in this work is group contribution method based on the Vogel–Tamman–Fulcher equation, [22]

$$\ln \eta = \frac{A_\eta + B_\eta}{T - T_{0\eta}} \quad (3)$$

where η is viscosity; T is temperature in K; and A_η , B_η and $T_{0\eta}$ are adjustable parameters. For $T_{0\eta}$ a constant value of 165.06 K is used for all the ionic liquids. The A_η and B_η can be obtained by a group contribution method with parameters available in Ref. [22].

As shown in Fig. 4, the two methods described above for the prediction of viscosity produce a good description of the viscosities of the ionic liquids up to $[C_9\text{mim}][\text{Ntf}_2]$. However, due to the non-linearity of the viscosity dependence with the chain length, shown in Fig. 1 and discussed before in this work, the group contribution models present, as expected, important deviations for heavy ionic liquids.

4. Conclusions

Viscosities of almost all members of the 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide family were reported in the temperature range between 278.15 and 393.15 K. At any given temperature, an increase in the alkyl side-chain length of the cation produces an increase in viscosity and a decrease in density of the ionic liquid. Temperature has a profound effect on the viscosities and the corresponding trends have been successfully fitted to the Vogel–Tamman–Fulcher equation. Several viscosity predictive methods were tested. Deviations found between reported values from different laboratories are mainly a consequence of both/either the presence of impurities (variable water and halide content) and/or an inadequate temperature control.

Acknowledgements

The authors are thankful for financial support from Fundação para a Ciência e a Tecnologia (Project PTDC/EQU-FTT/102166/2008). MT and PJC acknowledge the financial support from Fundação para a Ciência e a Tecnologia through their Post-doctoral (SFRH/BPD/34146/2006) and PhD (SFRH/BD/41562/2007) grants, respectively.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.fluid.2010.10.018.

References

- [1] M.J. Earle, J.M.M.S. Esperanca, M.A. Gilea, J.N.C. Lopes, L.P.N. Rebelo, J.W. Magee, K.R. Seddon, J.A. Widegren, *Nature* 439 (2006) 831–834.
- [2] Y.U. Paulechka, Dz.H. Zaitsau, G.J. Kabo, A.A. Strechen, *Thermochim. Acta* 439 (2005) 158–160.
- [3] M. Kosmulski, J. Gustafsson, J.B. Rosenholm, *Thermochim. Acta* 412 (2004) 47–53.
- [4] K. Ui, K. Yamamoto, K. Ishikawa, T. Minami, K. Takeuchi, M. Itagaki, K. Watanabe, N. Koura, *J. Power Sources* 183 (2008) 347–350.
- [5] K. Kubota, T. Nohira, T. Goto, R. Hagiwara, *Electrochem. Commun.* 10 (2008) 1886–1888.
- [6] T. Welton, *Chem. Rev.* 99 (1999) 2071–2084.
- [7] S. Ahrens, A. Peritz, T. Strassner, *Angew. Chem. Int. Ed.* 48 (2009) 7908–7910.
- [8] D.C. Forbes, A.M. Law, D.W. Morrison, *Tetrahedron. Lett.* 47 (2006) 1699–1703.
- [9] J. Jacquemin, P. Husson, A.A.H. Padua, V. Majer, *Green Chem.* 8 (2006) 172–180.
- [10] S. Tiwari, A. Kumar, *Angew. Chem. Int. Ed.* 118 (2006) 4942–4943.
- [11] S.V. Dzyuba, R.A. Bartsch, *Chem. Phys. Chem.* 3 (2002) 161–166.
- [12] H. Tokuda, S. Tsuzuki, M.A.B.H. Susan, K. Hayamizu, M. Watanabe, *J. Phys. Chem. B* 110 (2006) 19593–19600.
- [13] M. Tariq, A.P. Serro, J.L. Mata, B. Saramago, J.M.M.S. Esperanca, J.N.C. Lopes, L.P.N. Rebelo, *Fluid Phase Equilib.* 294 (2010) 131–138.
- [14] K.R. Seddon, A. Stark, M.J. Torres, *Pure Appl. Chem.* 72 (2000) 2275–2287.
- [15] J.A. Widegren, J.W. Magee, *J. Chem. Eng. Data* 52 (2007) 2331–2338.
- [16] K.R. Harris, M. Kanakubo, L.A. Woolf, *J. Chem. Eng. Data* 52 (2007) 1080–1085.
- [17] A. Ahosseini, A.M. Scurto, *Int. J. Thermophys.* 29 (2008) 1222–1243.
- [18] O.O. Okoturo, T.J. Vander Noot, *J. Electroanal. Chem.* 568 (2004) 167–181.
- [19] L.M.N.B.F. Santos, J.N.C. Lopes, J.A.P. Coutinho, J.M.S.S. Esperanca, L.R. Gomes, I.M. Marrucho, L.P.N. Rebelo, *J. Am. Chem. Soc.* 129 (2007) 284–285.
- [20] J.N.C. Lopes, A.A.H. Padua, *J. Phys. Chem. B* 108 (2004) 16893–16898.
- [21] H. Matsuda, H. Yamamoto, K. Kurihara, K. Tochigi, *J. Comput. Aided Chem.* 8 (2007) 114–127.
- [22] R.L. Gardas, J.A.P. Coutinho, *AIChE J.* 55 (2009) 1274–1290.
- [23] M.S. Kelkar, E.J. Maginn, *J. Phys. Chem. B* 111 (2007) 4867–4876.
- [24] X. Paredes, O. Fandiño, M.J.P. Comuñas, A.S. Pensado, J. Fernández, *J. Chem. Thermodyn.* 41 (2009) 1007–1015.
- [25] P.J. Carvalho, T. Regueira, L.M.N.B.F. Santos, J. Fernandez, J.A.P. Coutinho, *J. Chem. Eng. Data* 55 (2010) 645–652.
- [26] A.P. Froba, H. Kremer, A. Leipetz, *J. Phys. Chem. B* 112 (2008) 12420–12430.
- [27] J.M. Crosthwaite, M.J. Muldoon, J.K. Dixon, J.L. Anderson, J.F. Brennecke, *J. Chem. Thermodyn.* 37 (2005) 559–568.
- [28] S. Carda-Broch, A. Berthod, D.W. Armstrong, *Anal. Bioanal. Chem.* 375 (2003) 191–199.
- [29] J.M. Slattery, C. Daguene, P.J. Dyson, T.J.S. Schubert, I. Crossing, *Angew. Chem. Int. Ed.* 46 (2007) 5384–5388.
- [30] G. McHale, C. Hardacre, R. Ge, N. Doy, R.W.K. Allen, J.M. MacInnes, M.R. Bown, M.I. Newton, *Anal. Chem.* 80 (2008) 5806–5811.
- [31] A.B. McEwen, H.L. Ngo, K. LeCompte, J.L. Goldman, *J. Electrochem. Soc.* 146 (1999) 1687–1695.
- [32] D. Morgan, L. Ferguson, P. Scovazzo, *Ind. Eng. Chem. Res.* 44 (2005) 4815–4823.
- [33] M. Tariq, I.M. Marrucho, J.N. Canongia Lopes, L.P.N. Rebelo, Viscosity and Conductivity of [C₄mim][NTf₂], [C₄mim][dca], [C₂mim][EtOSO₃] and [aliquat][dca], (in preparation).
- [34] P. Bonhote, A.P. Dias, N. Papageorgiou, K. Kalyanasundaram, M. Gratzel, *Inorg. Chem.* 35 (1996) 1168–1178.
- [35] S. Kitaoka, K. Nobuoka, Y. Ishikawa, *Tetrahedron* 61 (2005) 7678–7685.
- [36] J.G. Huddleston, A.E. Visser, W.M. Reichert, H.D. Willauer, G.A. Broker, R.D. Rogers, *Green Chem.* 3 (2001) 156–164.
- [37] N.V. Ignatev, U. Welz-Biermann, A. Kucheryna, G. Bissky, H. Willner, *J. Fluorine Chem.* 126 (2005) 1150–1159.
- [38] M.E. Kandil, K.N. Marsh, *J. Chem. Eng. Data* 52 (2007) 2382–2387.
- [39] K.N. Marsh, J.F. Brennecke, R.D. Chirico, M. Frenkel, A. Heintz, J.W. Magee, C.J. Peters, L.P.N. Rebelo, K.R. Seddon, *Pure Appl. Chem.* 81 (2009) 781–790.
- [40] F.J.V. Santos, C.A. Nieto de Castro, P.J.F. Mota, A.P.C. Ribeiro, *Int. J. Thermophys.* (2010). doi:10.1007/s10765-009-r0584-4.
- [41] D. Almantariotis, T. Gefflaut, A.A.H. Padua, J.Y. Coxam, M.F.C. Gomes, *J. Phys. Chem. B* 114 (2010) 3608–3617.
- [42] A.E. Andreatta, A. Arce, E. Rodil, A. Soto, *J. Chem. Thermodyn.* 41 (2009) 1317–1323.
- [43] Q. Gan, M. Xue, D. Rooney, *Sep. Purif. Technol.* 51 (2006) 185–192.
- [44] J.N.A.C. Lopes, A.A.H. Padua, *J. Phys. Chem. B* 110 (2006) 3330–3335.
- [45] A. Triolo, O. Russina, H.J. Bleif, E. Di Cola, *J. Phys. Chem. B* 111 (2007) 4641–4644.
- [46] R.C. Reid, J.M. Prausnitz, T.K. Sherwood, *The Properties of Gases and Liquids*, fourth ed., McGraw-Hill, New York, 1987.
- [47] A.J. Queimada, I.M. Marrucho, J.A.P. Coutinho, E.H. Stenby, *Int. J. Thermophys.* 26 (2005) 47–61.
- [48] R.L. Gardas, J.A.P. Coutinho, *Fluid Phase Equilib.* 266 (2008) 195–201.