

Short communication

A group contribution method for viscosity estimation of ionic liquids

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Abstract

Based on experimental viscosity data collected from the literature and using density data obtained from a predictive method previously proposed by the authors, a group contribution method is proposed to estimate viscosity of imidazolium-, pyridinium-, and pyrrolidinium-based ILs containing hexafluorophosphate (PF₆), tetrafluoroborate (BF₄), bis(trifluoromethanesulfonyl) amide (Tf₂N), chloride (Cl), acetate (CH₃COO), methyl sulfate (MeSO₄), ethyl sulfate (EtSO₄), and trifluoromethanesulfonate (CF₃SO₃) anions, covering wide ranges of temperature, 293–393 K and viscosity, 4–21,000 cP. It is shown that a good agreement with literature data is obtained. For circa 500 data points of 29 ILs studied, a mean percent deviation (MPD) of 7.7% with a maximum deviation smaller than 28% was observed. 71.1% of the estimated viscosities present deviations smaller than 10% of the experimental values while only 6.4% have deviations larger than 20%. The group contribution method here developed can thus be used to evaluate the viscosity of new ionic liquids in wide ranges of temperatures at atmospheric pressure and, as data for new groups of cations and anions became available, can be extended to a larger range of ionic liquids.

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Keywords: Ionic liquid; Viscosity; Density; Group contribution method

Abbreviations: IL, ionic liquid; MPD, mean percentage deviation; CAMD, computer aided molecular design; CSGC, corresponding-states group-contribution; O.F., objective function; [C₄mim][PF₆], 1-butyl-3-methylimidazolium hexafluorophosphate; [C₆mim][PF₆], 1-hexyl-3-methylimidazolium hexafluorophosphate; [C₈mim][PF₆], 1-octyl-3-methylimidazolium hexafluorophosphate; [C₂mim][BF₄], 1-ethyl-3-methylimidazolium tetrafluoroborate; [C₃mim][BF₄], 1-propyl-3-methylimidazolium tetrafluoroborate; [C₄mim][BF₄], 1-butyl-3-methylimidazolium tetrafluoroborate; [C₆mim][BF₄], 1-hexyl-3-methylimidazolium tetrafluoroborate; [C₈mim][BF₄], 1-octyl-3-methylimidazolium tetrafluoroborate; [C₂mim][Tf₂N], 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide; [C₄mim][Tf₂N], 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide; [C₆mim][Tf₂N], 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide; [C₈mim][Tf₂N], 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide; [C₆mim][Cl], 1-hexyl-3-methylimidazolium chloride; [C₈mim][Cl], 1-octyl-3-methylimidazolium chloride; [C₄mim][CH₃COO], 1-butyl-3-methylimidazolium acetate; [C₁mim][MeSO₄], 1,3-dimethylimidazolium methylsulfate; [C₄mim][MeSO₄], 1-butyl-3-methylimidazolium methylsulfate; [C₂mim][EtSO₄], 1-ethyl-3-methylimidazolium ethylsulfate; [C₂mim][CF₃SO₃], 1-ethyl-3-methylimidazolium trifluoromethanesulfonate; [C₄mim][CF₃SO₃], 1-butyl-3-methylimidazolium trifluoromethanesulfonate; [C₄py][Tf₂N], 1-butylpyridinium bis(trifluoromethylsulfonyl)imide; [C₆py][Tf₂N], 1-hexylpyridinium bis(trifluoromethylsulfonyl)imide; [C₄mpy][Tf₂N], 1-butyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide; [C₈mpy][Tf₂N], 1-hexyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide; [C₄mpy][BF₄], 1-butyl-3-methylpyridinium tetrafluoroborate; [C₂py][EtSO₄], 1-ethylpyridinium ethylsulfate; [C₂mpy][EtSO₄], 1-ethyl-3-methylpyridinium ethylsulfate; [C₄mpyr][Tf₂N], 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide; [C_nmim]⁺, 1-alkyl-3-methylimidazolium cation; [C_nmpy]⁺, 1-alkyl-3-methylpyridinium cation; [C_nmX]⁺, 1-alkyl-3-methyl(imidazolium or pyridinium) cation.

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1. Introduction

Ionic liquid (IL) synthesis, characterization, properties, and applications are rapidly growing areas of the current research interest. ILs have been accepted as “green-chemicals” which excited both the academia and the chemical industries. ILs result from the combination of several organic cations and inorganic or organic anions. The wide range of combinations of cation and anion for ILs allow a great variety of tunable interactions and applications. ILs received an advantageous edge in various applications due to their unique properties, like negligible volatility, wide liquidus range, non-flammability, high thermal conductivity, chemical and physical stability, and high potential for recycling.

Development of ionic liquids for specific tasks is currently being pursued by many researchers as the large number of cation/anion combinations makes possible to produce ionic liquids with a set of desired properties. With the increasing availability of experimental data and their quality, the development of predictive methods for IL properties and Computer Aided Molecular Design (CAMD) of IL becomes possible.

Viscosity describes a fluid’s internal resistance to flow and may be thought of as a measure of fluid friction. Viscosity information of fluids and their mixtures is essential for the design of heat-transfer equipment, process piping, reactors, stripping columns, deodorizers, liquid–liquid extractors, distillation columns, crystallization equipment, and other units found in various chemical, oil, paint, clay, dairy and food industry. Because viscosity strongly affects flow behavior, it must be considered in engineering process calculations, analysis and design, being also an input for process simulation and optimization.

Viscosity is an important physical property of ionic liquids. A low viscosity is generally desired to use IL as a solvent, to minimize pumping costs and increase mass transfer rates while higher viscosities may be favorable for other applications such as lubrication or use in membranes. It is known that the viscosity of ILs vary widely depending on the type of cation and anion. The viscosities of ILs are relatively high compared to those of common organic solvents. Organic solvents typically have room temperature viscosities ranging from 0.2 to 10 cP [1] whereas ILs display a broad range of room temperature viscosities, from 10 to greater than 10⁵ cP [2]. Experimental data for viscosity of ionic liquids is still scarce and limited to a few classes of well-researched ionic liquids. More viscosity data and better understanding of this property are required for developing ionic liquids for a specific purpose, and if experimentally measured viscosity data are not available, theoretical or empirical methods must be used to establish if the viscosities are within acceptable limiting values defined in the design specifications. For this purpose prediction methods for viscosity of ILs are required.

While much work has been devoted to the wide range of applications of ILs, the basic understanding and study of their structure–property relationships is of equivalent importance but has lagged behind. More specifically, studies on how the structure of the ions in the IL influences their physical properties are rare. Knowledge of the structure–property relationship is important for assessing the suitability of ILs for specific applications,

as well as the design of new ILs. Very few works have systematically studied the qualitative and/or quantitative relationships between the structures of ILs and their fundamental properties [3–7], such as melting point, viscosity, density, surface tension, thermal and electrochemical stability, solvent properties, and speed of sound. At present, however, data for many other physico-chemical properties of ionic liquids are in short supply, or too unreliable to allow similar structure–property relationship studies.

We already succeeded in developing rapid predictive methods for density [8] in wide ranges of temperature and pressure, and surface tension [9] and speed of sound [10] of ILs in a wide temperature range and at atmospheric pressure. In continuation of our studies on the development of predictive methods for physical properties of ILs, a model for prediction of viscosities of ionic liquids will be proposed and it will be shown that it allows a good description of the experimental viscosities available.

2. Results and discussion

A data base of experimental viscosities (η) available in the open literature was collected and is reported in Table 1. A global number of 498 data points for 29 ILs based on imidazolium-, pyridinium-, and pyrrolidinium cations with hexafluorophosphate (PF₆), tetrafluoroborate (BF₄), bis(trifluoromethanesulfonyl) amide (Tf₂N), chloride (Cl), acetate (CH₃COO), methyl sulfate (MeSO₄), ethyl sulfate (EtSO₄), or trifluoromethanesulfonate (CF₃SO₃) as anions, covering wide ranges of temperature, 293.15–393.15 K and viscosity, 4–21,000 cP [2,11–43], were used in this study.

Many estimation methods for the viscosity of pure components and mixtures are available in literature reviews and books [44–51]. The most useful viscosity estimation methods for complex molecules for which limits information besides they molecular structure is available are generally based on group contribution (e.g., the Orrick–Erbar method [45], the Sastry–Rao method [52], and the UNIFAC-VISCO method [53]), the corresponding states concept (e.g., Przedzicki and Sridhar [54], Chatterjee and Vasant [55], Teja and Rice [56,57], and Queimada et al. [58,59]) or the corresponding-states group-contribution (CSGC) method (e.g., Yinghua et al. [60]). Group contribution methods for the estimation of liquid viscosity usually use some variation of temperature dependence proposed by de Guzman [61], known as the Andrade equation [62].

In the present work, the viscosity of ionic liquids is estimated using an Orrick–Erbar-type approach [45]. The method here proposed employs a group contribution technique to estimate the *A* and *B* parameters in the following equation:

$$\ln \frac{\eta}{\rho M} = A + \frac{B}{T} \quad (1)$$

where η and ρ are the viscosity in cP units and density in g cm^{−3} units, respectively. *M* is the molecular weight and *T* is the absolute temperature. The group contributions to calculate *A* and *B* parameters for ILs are given in Table 2. Orrick and Erbar [45] tested their method for 188 organic liquids with average devia-

Table 1
 Prediction of viscosity of imidazolium-, pyridinium-, and pyrrolidinium-based ionic liquids

Ionic liquid	M (g mol ⁻¹)	Molecular volume (Å ³)	Temperature range (K)	Data points	Percent deviation (range) (%)	Mean percent deviation (%)	Reference
[C ₄ mim][PF ₆]	284.18	345	293.15–353.15	16	-7.88; 9.29	4.28	[11]
			293.15–353.15	4	-8.59; 7.28	6.06	[12]
			293.1–353.1	8	0.01; 20.62	11.78	[13]
			293.15–323.15	7	3.69; 17.55	13.41	[14]
[C ₆ mim][PF ₆]	312.24	401	293.15–323.15	7	-15.17; 0.00	5.17	[14]
			293.15–353.15	11	-4.59; -18.57	10.19	[15]
			293.15–303.15	2	-11.58; -15.56	13.57	[16]
[C ₈ mim][PF ₆]	340.29	457	298.1	1	-0.35	0.35	[17]
			293.15–323.15	7	-6.22; 3.23	3.33	[14]
			293.15–343.15	11	-1.47; -12.43	5.88	[18]
			293.15–353.15	4	-0.23; -17.33	8.17	[19]
			293.15–303.15	2	8.19; 9.53	8.86	[16]
			293.15–303.15	2	9.27; 16.43	12.85	[20]
[C ₂ mim][BF ₄]	197.97	255	293.1	1	12.41	12.41	[16]
[C ₃ mim][BF ₄]	212.00	283	298.1	1	-23.22	23.22	[21]
[C ₄ mim][BF ₄]	226.03	311	298.1	1	0.04	0.04	[22]
			293.15–353.15	31	-12.07; 9.58	5.24	[23]
			293.15–323.15	7	-8.39; 8.64	5.85	[24]
			293.15–323.15	6	-7.52; 11.48	6.32	[25]
			293.67–388.04	11	-7.61; 13.26	8.30	[26]
			293.15–353.15	4	-5.41; 12.71	8.39	[12]
			293.1–353.1	8	-8.13; 16.29	10.03	[13]
			293.1–303.1	2	-10.34; -10.71	10.52	[16]
[C ₆ mim][BF ₄]	254.08	367	293.15–323.15	7	-10.08; 1.31	3.01	[24]
[C ₈ mim][BF ₄]	282.13	423	293.15–353.15	15	-12.59; -25.87	16.89	[18]
			293.15–323.15	7	16.24; 21.48	19.36	[24]
[C ₂ mim][Tf ₂ N]	391.32	430	293.15	1	-1.15	1.15	[2]
			293.15–353.15	7	-7.04; 0.84	2.08	[27]
			303.15	1	-3.27	3.27	[28]
			298.15	1	3.58	3.58	[29]
			293–343	7	-8.97; 3.73	3.73	[30]
			293.15–353.15	7	-13.78; 0.78	3.91	[31]
			293.1–353.1	8	-1.79; -13.25	5.95	[13]
			293.39–388.19	11	-5.84; -16.79	9.24	[26]
			[C ₄ mim][Tf ₂ N]	419.37	486	293.15	1
293.40–387.51	11	-0.58; -11.38				2.85	[26]
293.15–353.15	7	-14.64; 2.41				4.02	[31]
293.1–353.1	8	-14.97; 0.99				4.48	[13]
293.15–353.15	13	-1.69; -16.19				5.48	[15]
303.15	1	-5.92				5.92	[32]
293.15–363.15	15	5.20; 7.08				6.22	[33]
[C ₆ mim][Tf ₂ N]	447.42	542	293.1–353.1	8	-5.39; 6.71	3.55	[13]
			293–343	7	-3.69; 6.45	4.01	[30]
			293.15–373.15	12	-17.12; 4.71	5.02	[34]
			293.15–353.15	7	-1.98; 11.00	6.26	[31]
			293.15–393.15	14	-24.39; 8.21	6.47	[19]
[C ₈ mim][Tf ₂ N]	475.48	598	293.15–353.15	7	-0.44; 22.77	14.58	[31]
			293.1–353.1	8	1.06; 21.47	15.44	[13]
[C ₆ mim][Cl]	202.73	341	298.15–343.15	4	-27.75; 1.41	10.53	[36]
[C ₈ mim][Cl]	230.78	397	298.15–343.15	4	5.99; 27.61	17.07	[36]
[C ₄ mim][CH ₃ COO]	170.21	323.5	293–343	7	-12.63; 8.00	5.92	[30]
[C ₁ mim][MeSO ₄]	208.24	270	293.15–343.15	7	5.63; 16.53	11.33	[20]
[C ₄ mim][MeSO ₄]	250.32	354	293.15–343.15	9	-12.05; -26.00	16.49	[37]

Table 1 (Continued)

Ionic liquid	M (g mol ⁻¹)	Molecular volume (Å ³)	Temperature range (K)	Data points	Percent deviation (range) (%)	Mean percent deviation (%)	Reference
[C ₂ mim][EtSO ₄]	236.29	326	298.15	1	-3.01	3.01	[38]
			298.15	1	-3.01	3.01	[39]
			298.15–348.15	6	-1.87; 9.84	5.65	[40]
			298.15–328.15	3	-0.20; 8.66	5.69	[41]
			298.15–343.15	10	-0.20; 9.36	6.27	[42]
			296.80–388.19	11	-22.14; 6.19	7.61	[26]
[C ₂ mim][CF ₃ SO ₃]	260.24	311	298.15–348.15	6	3.93; 22.19	16.19	[40]
[C ₄ mim][CF ₃ SO ₃]	288.29	367	293.15–323.15	6	-6.54; 3.05	2.75	[25]
			293.15	1	3.05	3.05	[2]
			293.1–353.1	8	-17.17; 1.11	5.00	[13]
[C ₄ py][Tf ₂ N]	416.37	478	293.1–353.1	8	-19.33; 7.25	8.45	[13]
[C ₆ py][Tf ₂ N]	444.42	534	293–343	7	-7.73; 10.21	6.25	[30]
[C ₄ mpy][Tf ₂ N]	430.39	513	293–343	7	-14.71; 0.60	5.80	[30]
[C ₆ mpy][Tf ₂ N]	458.45	569	293–343	7	-0.56; 10.08	5.70	[30]
[C ₈ mpy][Tf ₂ N]	486.50	625	293–343	6	9.85; 23.47	19.46	[30]
[C ₄ mpy][BF ₄]	237.05	338	298–343	6	-2.07; -27.12	11.75	[30]
[C ₂ py][EtSO ₄]	233.29	318	293–343	7	-25.08; 1.72	9.35	[30]
[C ₂ mpy][EtSO ₄]	247.32	353	293–343	7	-23.80; 1.82	8.44	[30]
[C ₄ mpyr][Tf ₂ N]	422.41	501	293.1–353.1	8	-16.32; 1.11	6.06	[13]
			301.0–343.0	6	-6.38; 26.31	11.60	[43]
Total			293.15–393.15	498	-27.75; 27.61	7.78	

tion of 15%, but percent errors in calculated viscosities varied widely (-63% to 60%). While Orrick and Erbar [45] used a fixed density value at 293 K, the model here proposed for ILs uses temperature dependent densities obtained from a predictive method previously developed by us [8] and found that by using temperature dependency instead of fixed density at 293 K, the overall mean percent deviation (MPD) is improved from 9.01% to 7.78%.

Recently, we proposed an extension of the Ye and Shreeve method [63] for the estimation of ionic liquid densities [8] in a wide range of temperatures 273.15–393.15 K and pressures 0.10–100 MPa, according to Eq. (2) that is here used in the estimation of the viscosity (η) using Eq. (1).

$$\rho = \frac{M}{NV(a + bT + cP)} \quad (2)$$

where ρ is the density in kg m⁻³, M is molecular weight in kg mol⁻¹, N is the Avogadro constant, V is the molecular volume in Å³, T is the temperature in K and P is the pressure in MPa. The coefficients a , b and c were estimated by fitting Eq. (2) to our previously published experimental data [64,65]. A total amount of circa 800 density data points were used. The values of coefficients a , b and c obtained are 0.8005 ± 0.0002 , $6.652 \times 10^{-4} \pm 0.007 \times 10^{-4} \text{ K}^{-1}$ and $-5.919 \times 10^{-4} \pm 0.024 \times 10^{-4} \text{ MPa}^{-1}$, respectively, at 95% confidence level. The mean percentage deviation (MPD) of calculated densities from the experimental densities is 0.29%. For the density calculation, molecular volumes (V) of ions and groups were either directly taken from literature [63] or calculated following the Jenkins' procedure [66]. Molecular volumes of ILs used are shown in Table 1.

Using the model described in Eq. (2) for the estimation of densities of ionic liquids, the experimental viscosities were correlated by minimizing the objective function (O.F.) to estimate

Table 2
Group contributions for parameters A and B in Eq. (1)

Species	A	B (K)
Cations		
1,3-Dimethylimidazolium (+)	6.56	1757.1
1-Methylpyridinium (+)	6.87	1703.6
1,1-Dimethylpyrrolidinium (+)	5.43	2233.3
Anions		
PF ₆ ⁻	-20.49	2099.8
BF ₄ ⁻	-18.08	1192.4
Tf ₂ N ⁻	-17.39	510.0
Cl ⁻	-27.63	5457.7
CH ₃ COO ⁻	-21.26	2742.0
MeSO ₄ ⁻	-19.46	1732.8
EtSO ₄ ⁻	-19.06	1587.3
CF ₃ SO ₃ ⁻	-17.72	905.6
Groups		
CH ₂	-0.63	250.4
CH ₃	-0.74	250.0

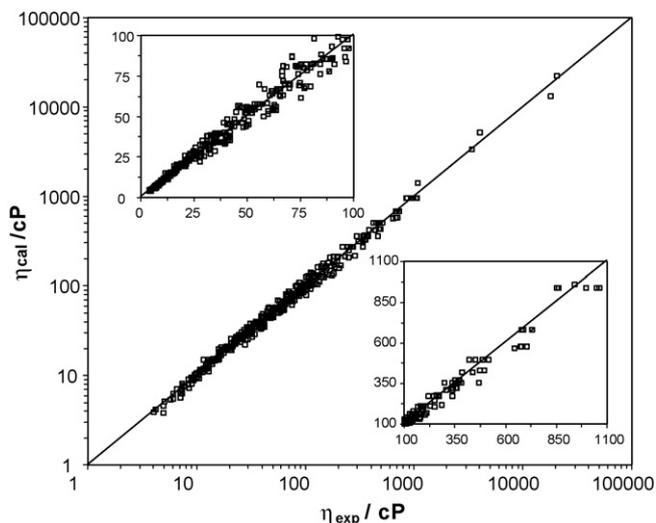


Fig. 1. Linear relationship between experimental and calculated viscosity using Eq. (1) for all ionic liquids in the current study.

the A and B parameters of Eq. (1),

$$\text{O.F.} = \frac{100 \times \sum_{i=1}^{N_p} |(\rho M \exp(A + (B/T)) - \eta_{\text{exp}}) \eta_{\text{exp}}|}{N_p} \quad (3)$$

According to Eq. (1), a plot of $\ln(\eta/\rho M)$ versus $1/T$ gives the values of B as slope and A as intercept. Similar plots were made for each IL studied and by the comparison of the A and B values of ILs having similar cation and anion estimates of the values of A and B for each cation and anion of ILs are produced. Then the cation is splitted into the heterocyclic ring, methylene and methyl group. From these initial estimates information for all the 498 viscosity data points available is used and the objective function (Eq. (3)) is minimized to obtain optimum values of the group parameter reported in Table 2.

The mean percent deviation (MPD) is defined as,

$$\text{MPD}(\%) = \frac{100 \times \sum_{i=1}^{N_p} |(\eta_{\text{cal}} - \eta_{\text{exp}}) / \eta_{\text{exp}}|}{N_p} \quad (4)$$

where N_p represents the number of data points were estimated for each system and are reported in Table 1.

The experimental viscosity data can be described with success, as shown in Fig. 1, by using a group contribution approach for parameters A and B (Table 2) for imidazolium-, pyridinium-, and pyrrolidinium-based ILs containing PF_6 , BF_4 , Tf_2N , Cl , CH_3COO , MeSO_4 , EtSO_4 , and CF_3SO_3 anions. The calculated viscosity (η_{cal}) of the ILs studied displays a good agreement with the corresponding experimental viscosity (η_{exp}), where $\ln \eta_{\text{cal}} = (0.9981 \pm 0.0011) \ln \eta_{\text{exp}}$ ($R^2 = 0.9994$ at 95% level of confidence). Relative deviations between the calculated and experimental viscosity data as a function of experimental viscosity for all data points used in the current study are shown in Fig. 2. For 498 data points of 29 ILs available in literature [2,11–43], the overall MPD is 7.78% with a maximum deviation smaller than 28%. From these 40.2% of the estimated viscosities were within an absolute deviation of 0.00–5.00%, 30.9% within 5.001–10.00%, 13.3% within 10.001–15.00%, 9.2% within 15.001–20.00%, and only 6.4%

of the estimated viscosities having larger than 20.0% deviation. The maximum absolute deviation is 27.75% for $[\text{C}_6\text{mim}][\text{Cl}]$ (1-hexyl-3-methylimidazolium chloride) at 298.15 K [36]. The largest deviations observed in predicted viscosities are mainly due to the large discrepancies in viscosity values reported in literature, which may be related to water content, halogen and other impurities present in IL samples, or the experimental method adopted. Due to the limited amount of experimental data currently available the rejection of doubtful experimental data was limited in the development of the proposed estimation method.

Small changes in the structure of the ILs can produce considerable differences in viscosity. A series of imidazolium based salts with various alkyl substituents and different anions was characterized in terms of viscosity in order to establish a relationship between chemical structure and physical properties [2], and it was suggested that the viscosity of ionic liquids is mainly controlled by hydrogen bonding, Van der Waal forces, molecular weight and mobility. To see the influence of the IL anion and temperature on the viscosity, estimations using Eq. (1), for the series of $[\text{C}_4\text{mim}]^+$ (1-butyl-3-methylimidazolium cation) with different anions, and $[\text{C}_4\text{mpy}]^+$ (1-butyl-3-methylpyridinium cation) with $[\text{BF}_4]$ and $[\text{Tf}_2\text{N}]$ anions at 298.15 and 323.15 K are presented in Fig. 3. The results indicate that the viscosity of ILs decreases markedly with increasing temperature. For example, $[\text{C}_4\text{mim}][\text{PF}_6]$ has a viscosity of 270.3 cP at 298.15 K, which decreases to 80.4 cP at 323.15 K and 23.5 cP at 353.15 K. For ILs having the imidazolium-cation, viscosity increases with anion in the order $[\text{Tf}_2\text{N}] < [\text{CF}_3\text{SO}_3] < [\text{BF}_4] < [\text{EtSO}_4] < [\text{MeSO}_4] < [\text{PF}_6] < [\text{CH}_3\text{COO}] < [\text{Cl}]$. ILs having highly symmetric or almost spherical anions are more viscous and viscosity is decreased for less symmetric anions. For ILs having a common anion and a similar alkyl chain length on the cation, it is observed that the viscosity increases with cation following the order: $[\text{Im}] < [\text{py}] < [\text{pyr}]$ as shown in Fig. 3. This is in agreement with the results of Crosthwaite et al. [30] that show that pyridinium salts are generally more viscous than the equivalent imidazolium salts. To see the

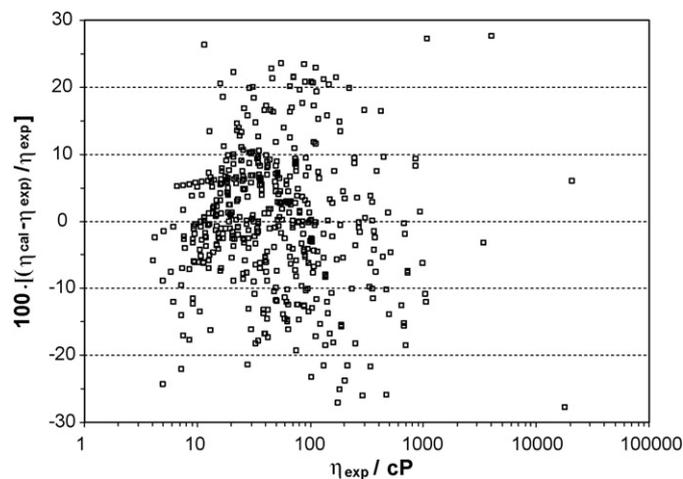


Fig. 2. Relative deviations between the calculated and experimental viscosity data as a function of experimental viscosity for all ionic liquids in the current study.

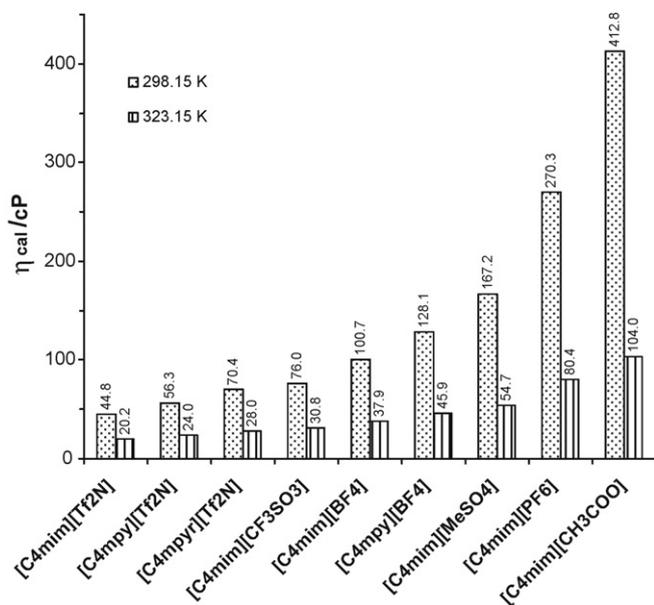


Fig. 3. Calculated viscosities of imidazolium and pyridinium based ILs with butyl chain length and different anions at 298.15 and 323.15 K.

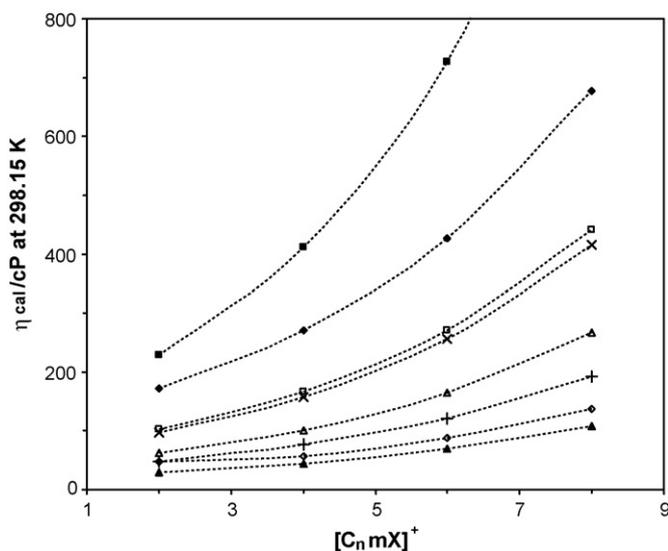


Fig. 4. Calculated viscosities of ionic liquids as a function of the number of carbons (n), on the series of $[C_n mX]^+$ (1-alkyl-3-methyl(imidazolium or pyridinium) cation) at 298.15 K: (Δ) $[C_n mX][PF_6]$; (\triangle) $[C_n mX][BF_4]$; (\blacktriangle) $[C_n mX][Tf_2N]$; (\blacksquare) $[C_n mX][CH_3COO]$; (\square) $[C_n mX][MeSO_4]$; (\times) $[C_n mX][EtSO_4]$; ($+$) $[C_n mX][CF_3SO_3]$; (\diamond) $[C_n mpy][Tf_2N]$.

influence of the alkyl chain length of IL cation on viscosity, the viscosity is calculated using Eq. (1), for the series of $[C_n mX]^+$ (1-alkyl-3-methylimidazolium cation) with different anions, and $[C_n mpy]^+$ (1-alkyl-3-methylpyridinium cation) with $[Tf_2N]$ anion at 298.15 K, and the data are plotted as a function of carbon numbers (n) on the series of $[C_n mX]^+$ in Fig. 4. The results indicate that the viscosity increases with alkyl chain length of imidazolium cation. For example, in the series of $[C_n mX][PF_6]$ with n equal to 2 to 8, the viscosity at 298.15 K increases monotonously from 172.3 to 677.4 cP. Viscosities for the series of $[C_n mpy][Tf_2N]$

ILs are slightly higher than those of $[C_n mX][Tf_2N]$ ILs. The increment with the alkyl chain length of imidazolium cation is more pronounced in case of ILs containing the $[Cl]$ anion, and seems to decrease with the symmetry of anion, showing the trend $[Cl] > [CH_3COO] > [PF_6] > [MeSO_4] > [EtSO_4] > [BF_4] > [CF_3SO_3] > [Tf_2N]$. More exhaustive and theoretically based studies are required to rationalize the different trends and to a more sound understanding of the trends here observed. Care is recommended when comparing or using viscosity data for ILs as differences among the results of several authors may be important since, as it is well known, the presence of small amounts of water or other impurities such as chloride seem to have a remarkable effect on the viscosity [16,67–71].

3. Conclusions

It is here shown that an Orrick–Erbar-type approach [45] was successfully applied to the development of a group contribution based method for the estimation of the viscosity of ILs. This group contribution method, along with a density correlation previously proposed by us [8], allows the description of viscosity for imidazolium-, pyridinium-, and pyrrolidinium-based ILs containing PF_6 , BF_4 , Tf_2N , Cl , CH_3COO , $MeSO_4$, $EtSO_4$, and CF_3SO_3 anions, in wide ranges of temperature, 293.15–393.15 K and viscosity, 4.1–20,883.0 cP. For a database of 498 data points for 29 ILs [2,11–43], the mean percent deviation (MPD) observed was of 7.78%. Literature show large discrepancies in viscosity data which yield higher deviations in calculated values. Calculated viscosities are in good agreement with experimental literature data. The model proposed here should be able to predict the viscosity of new ionic liquids in wide ranges of temperature and could be extended to a larger range of ionic liquids as data for these become available.

List of symbols

a, b, c	coefficients of density correlation
A, B	parameters in Eq. (1)
M	molecular weight
N	Avogadro constant
N_p	number of data points
P	pressure
T	temperature
V	molecular volume

Greek letters

η	viscosity
ρ	density

Subscripts

cal	calculated property
exp	experimental property

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