Density, Viscosity, and Surface Tension of Synthesis Grade Imidazolium, Pyridinium, and Pyrrolidinium Based Room Temperature Ionic Liquids

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Density, viscosity, and surface tension data sets of 13 ionic liquids formed by imidazolium, pyridinium, or pyrrolidinium cations paired with dicyanamide (DCA^-), tetrafluoroborate (BF_4^-), thiocyanate (SCN^-), methylsulfate ($MeSO_4^-$), and trifluoroacetate (TFA^-) anions are reported. The properties were measured at temperatures between (293 and 363) K. The effect of the ionic liquid forming anion and cation on the physical properties is analyzed systematically. As expected, the measured density, viscosity, and surface tension of the studied ionic liquids decreased with an increment in temperature. The density measurements were linearly correlated as a function of temperature, and the viscosities were fitted to a Vogel−Fulcher−Tamman equation. The density and surface tension data were used to estimate expansivity coefficients and surface thermodynamic properties of the ionic liquids. The physical properties are determined by the nature, size, and possible interactions of the ions forming the liquid. In general, ionic liquids with dicyanamide as anion exhibited lower densities and viscosities but a somewhat higher surface tension than all other ionic liquids used here. A longer alkyl chain in imidazolium-based ionic liquids was associated with lower density, higher viscosity, and lower surface tension.

Introduction

The use of room temperature ionic liquids (RTILs) is rapidly expanding into different application fields[1−15] including reaction media,[5−7] catalysis,[7−9] electrochemistry,[10] and separation processes.[11−15] The physical and chemical properties of the RTILs can be tailored by selecting the chemical structure of the cation and anion.[1−9] Knowledge of the properties of the RTILs is required for choosing a suitable liquid for each of their envisaged industrial applications. The physical properties such as density, viscosity, and surface tension are crucial for process engineering and equipment design. Additionally, complete data sets of RTIL properties are used for validating and improving molecular simulation and property prediction methods,[16−18] which later will be applied to process simulation and process development and design.

This work presents the density, viscosity, and surface tension of 13 RTILs measured at atmospheric pressure and at temperatures between (293 and 363) K. The liquids used here were selected to systematically study the influence of the anion and cation in the liquid properties. The liquids were all readily available from commercial suppliers. The screened ionic liquids included imidazolium, pyridinium, and pyrrolidinium cations paired with tetrafluoroborate, dicyanamide, thiocynanate, methylsulfate, or tetrafluoroborate anions. Densities, viscosities, and surface tension data are available for some of the 13 studied ionic liquids. The density,[19−27] viscosity,[20,21,26,27,48] and surface tension[30−34] of 1-butyl-3-methylimidazolium tetrafluoroborate can be found at temperatures between (293 and 343) K. Similarly, for 1-octyl-3-methylimidazolium tetrafluoroborate, the density,[24−26,46] viscosity,[26] and surface tension[30,33,34] measurements are reported. Some density[20,25] and viscosity[20,36] data of 1-butyl-3-methylimidazolium dicyanamide are available. Additionally, for 1-butyl-3-methylimidazolium thiocyanate, one density[50] measurement is available. The density and viscosity of 1-butyl-3-methylimidazolium methylsulfate[20,37,38] and *N*-butyl-4-methylpyridinium tetrafluoroborate[29,40] were also found in the literature. For the six ionic liquids previously mentioned, new density and viscosity measurements are presented, and the surface tension data sets are completed. The physical properties for the other seven studied RTILs have not been reported before.

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Experimental Section

Chemicals. The structures, CAS Registry Number (CAS-RN), and given acronym of the RTILs studied in this research are given in Table 1. The RTILs were obtained from different commercial suppliers.

The RTILs were first placed in a rotary evaporator (< 100 Pa) for at least 15 h and at 343 K to reduce their initial water content and other volatile compounds that may be present in the liquids. A Karl Fisher analysis was performed to determine the water content in the 1-butyl-3-methylimidazolium tetrafluoroborate ($[BMIM]BF_4$). In the rotary evaporator, the water mass fraction content of $[BMIM]BF_4$ was reduced from the initial as-received (1100 to about 100)$\cdot 10^{-6}$. The water content of all tested RTILs was obtained using a gravimetric microbalance (IGA 003 Hiden Isochema). A sample of (48 to 68) mg of each RTIL was placed in the gravimetric balance and heated at 343 K under vacuum (< 100 Pa) for a period of at least 12 h, until the changes in mass were in the order of 0.001 $mg\cdot h^{-1}$. As previously reported by Shiflett,[50] the main part of the mass loss corresponds to the water removed. The mass of a $[BMIM]BF_4$ sample decreased in the gravimetric balance from (56.0761 to 56.0677) mg with a mass fraction loss around $1\cdot 10^{-4}$, which is similar to the water mass fraction content obtained with the Karl Fisher analysis $100\cdot 10^{-6}$ for a sample previously dried in the rotary evaporator. The purity and water content of the used ionic liquids are presented below.

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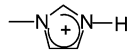
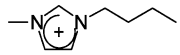
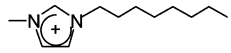
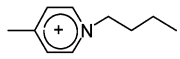
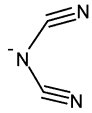
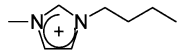
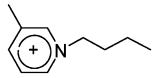
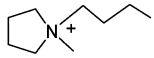
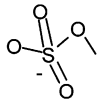
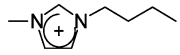
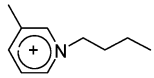
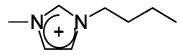
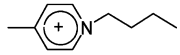
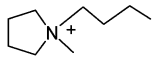
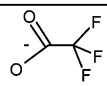
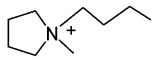
Table 1. Anion and Cation Structures of the Studied Room Temperature Ionic Liquids

RTIL	*Anion*	*Cation*
[MIM]BF_4 CAS RN: 151200-14-5		
[BMIM]BF_4 CAS RN: 174501-65-6		
[OMIM]BF_4 CAS RN: 244193-52-0		
[BMPy]BF_4 CAS RN: 343952-33-0		
[BMIM]DCA CAS RN: 448245-52-1		
[BMPy]DCA CAS RN: 712355-12-9		
[BMPyrr]DCA CAS RN: 370865-80-8		
[BMIM]$MeSO_4$ CAS RN: 401788-98-5		
[BMPy]$MeSO_4$ CAS RN: 916730-28-4		
[BMIM]SCN CAS RN: 344790-87-0		
[BMPy]SCN CAS RN: -		
[BMPyrr]SCN CAS RN: -		
[BMPyrr]TFA CAS RN: 712355-11-8		

1-Methylimidazolium Tetrafluoroborate ([MIM]BF_4). Synthesis quality purchased from Merck. Water and chloride (Cl^-) mass fraction contents were (< 10000 and < 1000)$\cdot 10^{-6}$, respectively. On the basis of the gravimetric data, the calculated water mass fraction content of a sample taken from the rotary evaporator was $\leq 480 \cdot 10^{-6}$.

1-Butyl-3-methylimidazolium Tetrafluoroborate ([BMIM]BF_4). High purity from Merck and 0.001 water mass fraction content. The water mass fraction content of the dry liquid was $100 \cdot 10^{-6}$, as determined by Karl Fischer titration.

1-Octyl-3-methylimidazolium Tetrafluoroborate ([OMIM]BF_4). Merck synthesis quality with water mass fraction content < $10000 \cdot 10^{-6}$. The water content of the dry sample calculated with the gravimetric data was $\leq 790 \cdot 10^{-6}$.

N-Butyl-4-methylpyridinium Tetrafluoroborate ([BMPy]BF_4). Merck synthesis quality with water content < $10000 \cdot 10^{-6}$. The water content of the dry liquid was $\leq 560 \cdot 10^{-6}$ mass fraction.

1-Butyl-3-methylimidazolium Dicyanamide ([BMIM]DCA). Merck grade purum $\geq$ 0.97 and water content $\leq 2000 \cdot 10^{-6}$. The dry water mass fraction content was $\leq 680 \cdot 10^{-6}$.

N-Butyl-3-methylpyridinium Dicyanamide ([BMPy]DCA). Merck for synthesis. Water and chloride (Cl^-) mass fraction contents were (< 10000 and < 1000)$\cdot 10^{-6}$, respectively. The calculated dry water mass fraction content of the liquid was $\leq 730 \cdot 10^{-6}$.

1-Butyl-1-methylpyrrolidinium Dicyanamide ([BMPyrr]DCA). Io-li-tec with mass fraction purity > 0.98. The water mass fraction content of the dry liquid was $\leq 570 \cdot 10^{-6}$.

1-Butyl-3-methylimidazolium Methylsulfate ([BMIM]$MeSO_4$). Produced by BASF and purchased from Fluka. Assay quality with mass fraction purity > 0.95. The dry water mass fraction content was $\leq 740 \cdot 10^{-6}$.

N-Butyl-3-methylpyridinium Methylsulfate ([BMPy]$MeSO_4$). Merck for synthesis. Water and chloride (Cl^-) mass fraction contents were (< 10000 and < 1000)$\cdot 10^{-6}$, respectively. The dry water mass fraction content was $\leq 1020 \cdot 10^{-6}$.

1-Butyl-3-methylimidazolium Thiocyanate ([BMIM]SCN). Produced by BASF and obtained from Sigma-Aldrich assay quality, mass fraction purity $\geq$ 0.95, water and chloride (Cl^-) mass fraction contents < $10000 \cdot 10^{-6}$. The calculated dry water mass fraction content was $\leq 260 \cdot 10^{-6}$.

1-Butyl-4-methylpyridinium Thiocyanate ([BMPy]SCN). Io-li-tec at purity > 0.98. After rotary evaporation, the dry water mass fraction content was $\leq 610 \cdot 10^{-6}$.

1-Butyl-1-methylpyrrolidinium Thiocyanate ([BMPyrr]SCN). Io-li-tec with mass fraction purity > 0.99. The calculated water content of the dry liquid was $\leq 390 \cdot 10^{-6}$ mass fraction.

1-Butyl-1-methylpyrrolidinium Trifluoroacetate ([BMPyr]TFA). Merck for synthesis with purity > 0.98. Water and chloride (Cl^-) contents were (< 10000 and < 1000)$\cdot 10^{-6}$ mass fraction, respectively. The dry water content was $\leq 650 \cdot 10^{-6}$ mass fraction.

Density Measurement. The density of all ionic liquids was measured at atmospheric pressure using a densimeter (Anton Paar DMA 5000). The densimeter was calibrated with a high purity water standard provided by Anton Paar. The density of the water standard was measured in the temperature range from (278.15 to 363.15) K and compared with the values reported in the densimeter instruction manual. The uncertainty in the density measurement is estimated to be $\pm\ 1 \cdot 10^{-4}$ $g \cdot cm^{-3}$. The temperature was controlled automatically by the desimeter within $\pm$ 0.001 K. The fitted viscosity correction of the densimeter was verified with acetone (Merck 98 %) and monoethylene glycol dimethyl ether (Fluka 99 %), which are liquids of known density and viscosity. The reported density measurements are the values corrected by the equipment for liquids with a viscosity lower than 700 mPa·s, with the exception of the density of [OMIM]BF_4 at 283 K, where the density value reported is the one obtained using the densimeter implemented correction for liquids with a viscosity larger than 500 mPa·s. The viscosity of [OMIM]BF_4 at 283 K was measured to be around 900 mPa·s. Previous to the density measurement, the RTILs were placed for 15 h in a vacuum rotary evaporator, at 373 K and < 100 Pa. A sample of the RTIL was taken from the rotary evaporator using a syringe and then injected in the densimeter cell, which was previously set at the measurement temperature. The cell of the densimeter was extensively cleaned and dried before each of the liquids was introduced. The presence of bubbles in the liquid when placed in the densimeter cell was not observed, and each measurement was replicated at least three times.

Viscosity Measurement. The kinetic viscosities of the ionic liquids were measured at atmospheric pressure using Ubbelohde-type viscometers purchased from Schott. Given the large range of viscosity and temperatures measured, three capillaries were used. The capillary diameters with a particular range of measurement of each viscometer were 0.63 mm (1.2 to 10)

$mm^2 \cdot s^{-1}$, 1.13 mm (10 to 100) $mm^2 \cdot s^{-1}$, and 2.01 mm (100 to 1000) $mm^2 \cdot s^{-1}$. During the measurements, the viscometer was placed in a heated water bath, and the temperature was regulated with a Lauda E 200 immersion heating thermostat (set point ± 0.1 K). The viscosity of tetraethylene glycol dimethyl ether (Fluka 98.0 %) was measured at a temperature range between (283 and 363) K as a reference in the viscometers certified by Schott. The time was measured using a VWR digital stopwatch with timing resolution of 0.01 s, and the estimated uncertainty in the time flow measurement is ± 0.1 s. The corresponding Hagenbach-Couette correction for each viscometer provided by the supplier was applied in the calculation of the kinematic viscosity. Absolute viscosities at each measured temperature were obtained with the corrected kinematic viscosity multiplied by the respective measured density of the liquid. The uncertainty in the absolute viscosity η is estimated to be ± 1 %. The RTIL samples used for measuring viscosity are the same as the ones that were prepared for the determination of density. Before each viscosity measurement and in addition to the earlier 15 h drying process, each RTIL liquid was previously kept in the rotary evaporator for a minimum of 4 h, brought to the desired measuring temperature, and then placed into the viscometer. The clean viscometer was flushed with argon gas to remove any traces of water in the system for about 20 min prior to filling with the ionic liquid. For all RTILs, the viscosity at each temperature was measured at least three times.

Surface Tension Measurement. The surface tension was measured with a Kruss K11 tensiometer using a ring. The ring of 9.545 mm radius was provided and certified by Kruss GmbH. The equipment parameters used during the measurements were: measuring speed between (0.4 and 3.0) $mm \cdot min^{-1}$, ring immersing speed from (80 to 100.0) $mm \cdot min^{-1}$, immersion depth from (2.0 to 3.0) mm, and probe sensitivity of 0.005 g. The value displayed in the tensiometer for each surface tension is a mean of a chosen number of immersion cycles of the ring. The number of immersion measurements for each determination was 15, and the maximum standard deviation from the mean value was set at 0.3 $mN \cdot m^{-1}$. The tensiometer has a resolution of 0.1 $mN \cdot m^{-1}$. The surface tension measurements were corrected using the Huh and Mason method already implemented in the tensiometer. The Huh and Mason correction has an error < 0.2 %. The surface tension of double distilled water and monoethylene glycol (99 %) was measured at temperatures from (283 to 363) K. The uncertainty of the surface tension measurements is ± 0.2 $mN \cdot m^{-1}$.

Traces of water and volatiles from the purchased liquids were removed in a rotary evaporator for 15 h at 373 K. To eliminate water and volatiles that may well contaminate the liquid sample while carrying the surface tension measurements, the tested samples were again placed in the rotary evaporator for at least 4 h, between each individual measurement. After that, the sample remained in the rotary evaporator, and the temperature was set to that desired for the measurement of the surface tension. Meanwhile, the temperature of the water bath connected to the thermostat vessel of the tensiometer was brought to the measurement temperature and kept constant (± 0.1 K) for 2 h. The ionic liquid sample was removed from the rotary evaporator and poured into a clean glass vessel in the tensiometer. Glass vessels of 70 mm diameter were used. The doors of the tensiometer chamber were closed; the temperature of the liquid was left to stabilize; and then the measurement was carried out. This procedure was repeated for each surface tension determination and each liquid sample. Once the process for measuring each surface tension was completed, the temperature at the surface of the liquid was measured using a digital thermometer with set point ± 0.01 K.

The humidity of the air can affect the surface tension measurements, especially the hygroscopic ones.[26] The water content of the ionic liquid equilibrates with that of the surrounding air. If a sample is gaining water, the surface tension at the same temperature measured with an interval of time is different. To ensure that the water removed at vacuum was not gained again during the measurement, the time allowed for the stabilization of the temperature once the sample was placed in the tensiometer should be as short as possible (≤ 5 min). When either temperature or water content at the surface was slightly changed with time, the measured surface tension was unstable and changed up to 2.0 $mN \cdot m^{-1}$ in a period of 15 min. To ensure that the liquid surface was stable, the largest variation allowed between two measurements taken 15 min apart at the same temperature was 0.3 $mN \cdot m^{-1}$. In total, for each temperature determination a minimum of three individual readings was taken.

Table 2. Density ρ of RTILs at T = (283.15 to 363.15) K and 0.1 MPa

	ρ/g·cm^{-3}			
T/K	[MIM]BF_4	[BMIM]BF_4	[OMIM]BF_4	[BMPy]BF_4
283.15		1.21309	1.11411	
293.15	1.38797	1.20570	1.10722	1.19298
303.15	1.37982	1.19838	1.10036	1.18606
313.15	1.37183	1.19118	1.09364	1.17930
323.15	1.36361	1.18406	1.08701	1.17252
333.15	1.35566	1.17703	1.08038	1.16577
343.15	1.34806	1.17006	1.07379	1.15903
353.15	1.33946	1.16316	1.06722	1.15233
363.15	1.33156	1.15630	1.06071	1.14565

	ρ/g·cm^{-3}			
T/K	[BMIM]DCA	[BMPy]DCA	[BMPyr]DCA	[BMPyr]TFA
293.15	1.06205	1.05171	1.11870	1.17574
303.15	1.05546	1.04564	1.11254	1.16877
313.15	1.04922	1.03962	1.10644	1.16182
323.15	1.04300	1.03365	1.10043	1.15492
333.15	1.03678	1.02773	1.09443	1.14807
343.15	1.03063	1.02186	1.08852	1.14127
353.15	1.02454	1.01604	1.08269	1.13450
363.15	1.01849	1.01026	1.07702	1.12772

	ρ/g·cm^{-3}				
T/K	[BMIM] SCN	[BMPy] SCN	[BMPyr] SCN	[BMIM] $MeSO_4$	[BMPyr] $MeSO_4$
293.15	1.07282	1.06436	1.03287	1.21018	1.21605
303.15	1.06691	1.05870	1.02761	1.20360	1.20946
313.15	1.06102	1.05302	1.02235	1.19706	1.20269
323.15	1.05518	1.04740	1.01710	1.19052	1.19626
333.15	1.04938	1.04180	1.01191	1.18401	1.18971
343.15	1.04363	1.03624	1.00673	1.17754	1.18329
353.15	1.03792	1.03071	1.00156	1.17110	1.17687
363.15	1.03225	1.02522	0.99643	1.16470	1.17024

Table 3. Constant for Equation 1 and Standard Error σ (Equation 3)

ionic liquid	$-A \cdot 10^4$	B	σ/g·cm^{-3}	range T/K
[MIM]BF_4	8.0465	1.6238		293 to 363
[BMIM]BF_4	7.0925	1.4135	$2.6 \cdot 10^{-4}$	283 to 363
[OMIM]BF_4	6.6670	1.3026	$1.8 \cdot 10^{-4}$	283 to 363
[BMPy]BF_4	6.7560	1.3909	$1.6 \cdot 10^{-4}$	293 to 363
[BMIM]DCA	6.2110	1.2438	$1.7 \cdot 10^{-4}$	293 to 363
[BMPy]DCA	5.9211	1.2251	$1.3 \cdot 10^{-4}$	293 to 363
[BMPyrr]DCA	5.9608	1.2932	$1.9 \cdot 10^{-4}$	293 to 363
[BMIM]SCN	5.7964	1.2426	$1.1 \cdot 10^{-4}$	293 to 363
[BMPy]SCN	5.5941	1.2283	$8.5 \cdot 10^{-5}$	293 to 363
[BMPyrr]SCN	5.2067	1.1854	$6.1 \cdot 10^{-5}$	293 to 363
[BMIM]$MeSO_4$	6.4998	1.4006	$7.5 \cdot 10^{-5}$	293 to 363
[BMPy]$MeSO_4$	6.5315	1.4074	$1.2 \cdot 10^{-4}$	293 to 363
[BMPyrr]TFA	6.8565	1.3766	$1.0 \cdot 10^{-4}$	293 to 363

In the determination of the surface tension of $[OMIM]BF_4$ and due to its manifest hygroscopicity, the inner space limited by the tensiometer doors was filled with nitrogen gas after the liquid sample was poured in the glass vessel and before the procedure for measuring the surface tension started to reduce the water content in the vicinity of the liquid surface. For the other RTILs, the flow of nitrogen into the measuring chamber did not have any noticeable impact on the stability of the measurements, therefore it was decided to carry out the surface tension measurement without nitrogen added and exposed to air. The measurements were carried out with a relative humidity of the air of (60 to 70) %.

Results and Discussion

Density. The measured densities of the RTILs at 0.1 MPa are listed in Table 2. At least three measurements were done at each temperature, and the tabulated density ρ corresponds to their arithmetic mean. The standard deviation (SD) of the density at each temperature was calculated with eq 1, where n is the number of measurements at each temperature. For all RTILs, the SD of the density at each measured temperature was smaller than $2.0 \cdot 10^{-5}$ g·cm^{-3}. The uncertainty in the density measurement was estimated to be $\pm\ 1 \cdot 10^{-4}$ g·cm^{-3}.

$$\mathrm{SD} = \left(\frac{\sum_{i}^{n} (\rho_i - \bar{\rho})^2}{n - 1} \right)^{1/2} \tag{1}$$

The density of all measured RTILs decreased when temperature was increased. The measured densities were linearly fitted as a function of temperature T according to eq 2, with a correlation coefficient $R^2 > 0.999$. The coefficients A and B of eq 2 and standard error of the linear fit σ are presented in Table 3, for each ionic liquid. The standard error of the linear fit is calculated using eq 3, where n is the total number of measurements.

$$\rho = A \cdot T + B \tag{2}$$

$$\sigma = \sqrt{\frac{1}{(n-2)} \cdot \left[\sum (\rho - \bar{\rho})^2 - \frac{[\sum (\rho - \bar{\rho}) \cdot (T - \bar{T})]^2}{(T - \bar{T})^2} \right]} \tag{3}$$

The measured density data compare well with reported literature values, which are available at the temperature range studied here for $[BMIM]BF_4$, $[OMIM]BF_4$, [BMIM]DCA, $[BMIM]MeSO_4$, and [BMPy]BF4.[40] Figure 1 shows the deviations between our experimental density data and those reported by other authors for $[BMIM]BF_4$, $[OMIM]BF_4$, [BMIM]DCA,

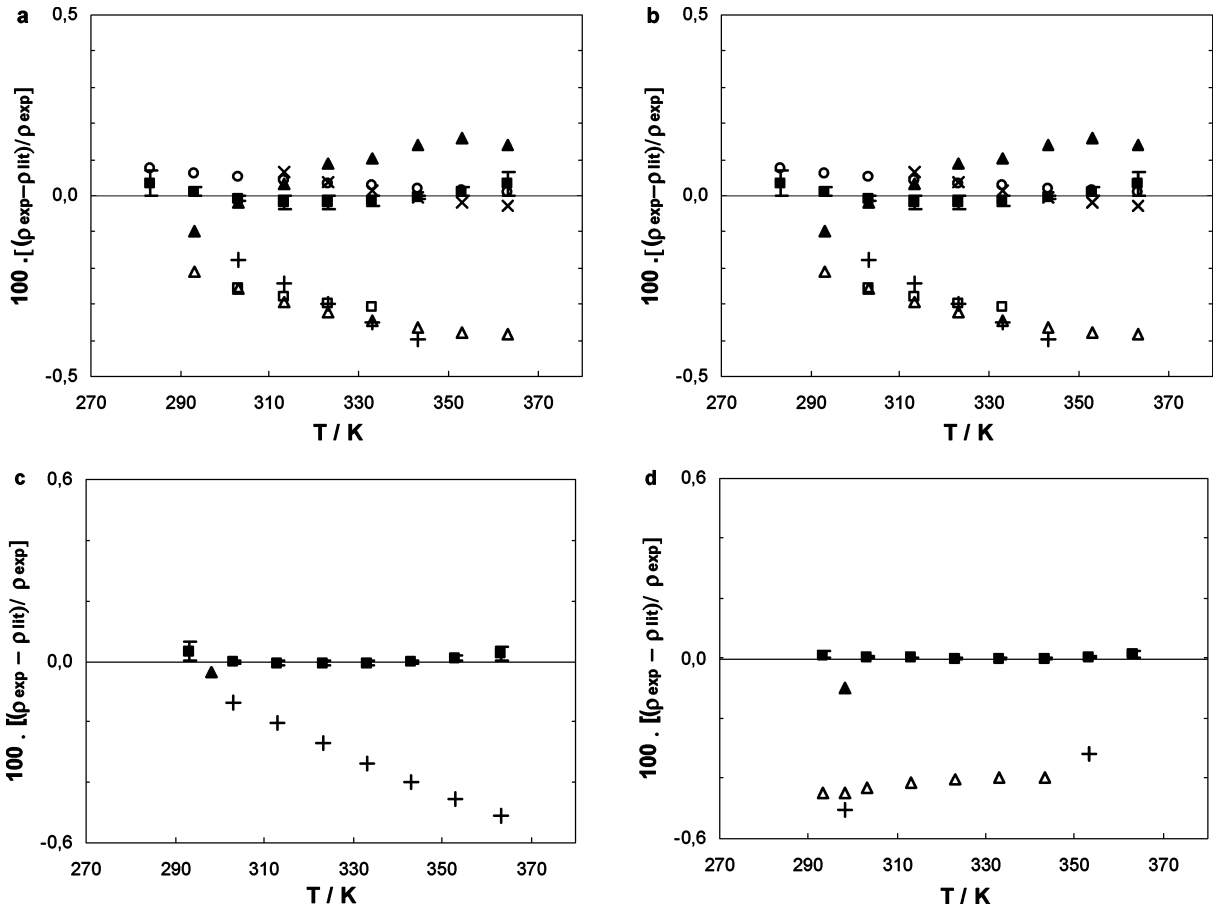


Figure 1. Relative deviations between the experimental density $\rho_{(exp.)}$ of the RTILs in this work and data reported in the literature $\rho_{(lit.)}$ as a function of temperature. ■, This work, deviation of the experimental densities of RTILs from the values obtained using eq 2 and error bars representing the uncertainty. Water mass fraction w is given where known. (a) $[BMIM]BF_4$ ($w = 100 \cdot 10^{-6}$): ▲, ref 24 ($w = 485 \cdot 10^{-6}$); ○, ref 21 ($w = (68 - 77) \cdot 10^{-6}$); ×, ref 22 ($w > 250 \cdot 10^{-6}$); △, ref 26 ($w = 307 \cdot 10^{-6}$); □, ref 23 ($w > 70 \cdot 10^{-6}$); +, ref 25 ($w = 1900 \cdot 10^{-6}$). (b) $[OMIM]BF_4$ ($w = 790 \cdot 10^{-6}$): ▲, ref 24 ($w = 371 \cdot 10^{-6}$); △, ref 26 ($w = 80 \cdot 10^{-6}$); +, ref 46 ($w = 6400 \cdot 10^{-6}$). (c) [BMIM]DCA ($w = 680 \cdot 10^{-6}$): ▲, ref 20 ($w = 256 \cdot 10^{-6}$); +, ref 25 ($w = 5150 \cdot 10^{-6}$). (d) $[BMIM]MeSO_4$ ($w = 740 \cdot 10^{-6}$): ▲, ref 20 ($w = 67 \cdot 10^{-6}$); △, ref 38 ($w > 300 \cdot 10^{-6}$); +, ref 37 ($w = 1000 \cdot 10^{-6}$).

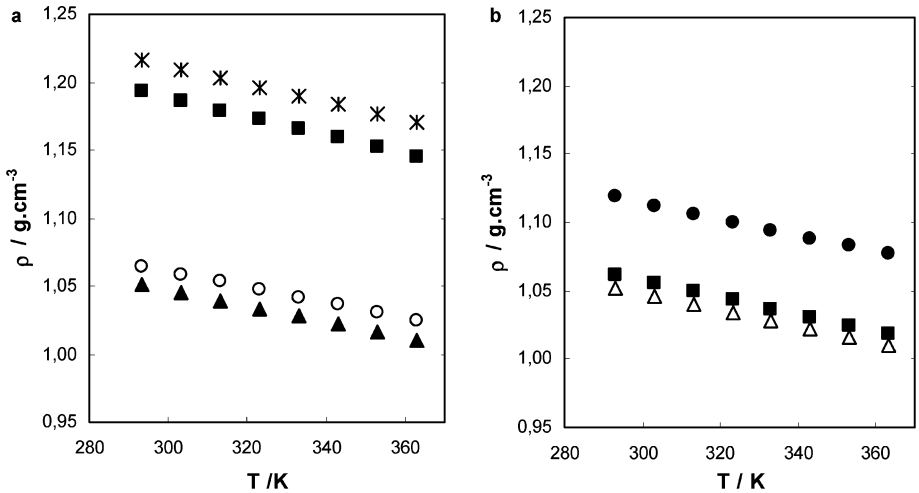


Figure 2. Density ρ of RTILs as a function of temperature at 0.1 MPa. (a) RTILs with pyridinium cation: ▲, [BMPy]DCA; ○, [BMPy]SCN; ■, [BMPy]BF_4; *, [BMPy]$MeSO_4$. (b) RTILs with DCA^- anion: △, [BMPy]DCA; ■, [BMIM]DCA; ●, [BMPy]DCA.

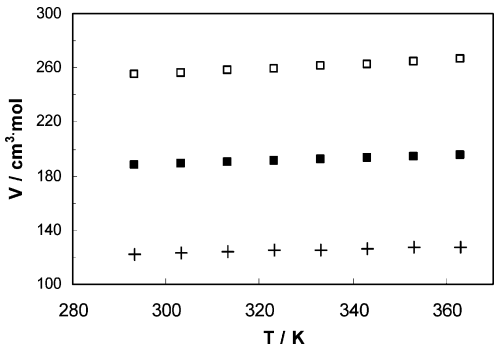


Figure 3. Molar volume V of the [R_1MIM]BF_4 ionic liquids as a function of temperature. Symbols: +, [MIM]BF_4; ■, [BMIM]BF_4; □, [OMIM]BF_4.

and [BMIM]$MeSO_4$. In the figure, the maximum deviation found is about 1.1 % for [OMIM]BF_4 with respect to Gu et al.[46] Figure 1 does not illustrate the deviation for [BMPy]BF_4, but the density of [BMPy]BF_4 was higher than the density measured by Bandres et al.[40] with a relative deviation of 0.6 %. In general, the deviations from our measurements and the values found in the literature range from (0.02 to 1.1) %. The deviations in density and other physical properties can be attributed to differences in the content of water and halides of the RTIL samples and also from the method of determination used.[23−31]

Effect of Anion and Cation Variation on the RTIL Density. Anion. The effect of the different anions on the liquid density of pyridinium-based ionic liquids is shown in Figure 2. The densities of the pyridinium-based ionic liquids are highest when paired with the methylsulfate anion closely followed by tetrafluoroborate and then by the thiocyanate anion. The lowest densities were observed with the dicyanamide anion. A similar trend is obtained for the densities of the imidazolium-based ionic liquids measured here.

Table 5. Viscosity η of the RTILs at T = (283.15 to 363.15) K and 0.1 MPa

[BMIM]BF_4		[OMIM]BF_4		[BMPy]BF_4	
T/K	$\eta \pm$ SD/mPa·s	T/K	$\eta \pm$ SD/mPa·s	T/K	$\eta \pm$ SD/mPa·s
283.15	248.1 ± 3.2	283.15	895.3 ± 4.6	298.15	202.8 ± 0.8
293.15	136.9 ± 1.2	293.15	447.6 ± 3.5	301.15	173.1 ± 0.2
303.15	79.5 ± 1.0	303.15	241.7 ± 2.4	305.15	134.7 ± 0.2
313.15	50.5 ± 0.7	313.15	141.2 ± 1.1	308.15	101.0 ± 0.2
323.15	34.1 ± 0.4	323.15	88.8 ± 0.9	318.15	62.3 ± 0.2
333.15	24.2 ± 0.3	333.15	57.7 ± 0.7	328.15	39.6 ± 0.1
343.15	17.9 ± 0.2	343.15	39.4 ± 0.4	338.15	26.8 ± 0.2
353.15	13.8 ± 0.2	353.15	28.1 ± 0.2	348.15	19.0 ± 0.2
363.15	10.7 ± 0.1	363.15	20.8 ± 0.2		

[BMIM]DCA		[BMPy]DCA	
T/K	$\eta \pm$ SD/mPa·s	T/K	$\eta \pm$ SD/mPa·s
293.15	33.2 ± 0.3	298.15	35.2 ± 0.1
303.15	24.4 ± 0.2	301.15	31.0 ± 0.1
313.15	16.8 ± 0.1	305.15	26.4 ± 0.1
323.15	12.4 ± 0.1	308.15	23.1 ± 0.1
333.15	8.9 ± 0.4	318.15	16.8 ± 0.2
343.15	6.6 ± 0.2	328.15	12.4 ± 0.3
353.15	4.7 ± 0.4	338.15	9.5 ± 0.2
363.15	3.8 ± 0.3	348.15	7.5 ± 0.2

Table 6. Best Fit Parameters for Equation 6

	A'/mPa·s	B'/K	T_o/K
[BMIM]BF_4	0.07601	1000.0	159.6
[OMIM]BF_4	0.02814	1440.0	144.2
[BMPy]BF_4	0.07246	905.3	184.3
[BMIM]DCA	0.05417	1000.0	138.0
[BMPy]DCA	0.21524	590.8	182.2

The density of ionic liquids with an imidazolium cation increases with increasing molecular weight of the anion.[25] The molecular weight of the anions increases as: $SCN^- < DCA^- < BF_4^- < MeSO_4^- < TFA^-$. However, for both imidazolium and pyridinium cations, the density of the ionic liquids with thiocianate as anion is higher than that of the ionic liquids with the dicyanamide anion. Similar behavior was observed by

Table 4. Thermal Expansion Coefficient $\alpha_p = -d(\ln \rho)/dT$ of the RTILs at 0.1 MPa

	$10^4\ \alpha_p/K^{-1}$				
	BF_4^-	DCA^-	SCN^-	$MeSO_4^-$	TFA^-
$[OMIM]^+$	6.12 ± 0.01				
$[BMIM]^+$	6.01 ± 0.01	5.97 ± 0.01	5.51 ± 0.01	5.47 ± 0.01	
$[MIM]^+$	5.92 ± 0.01				
$[BMPy]^+$	5.80 ± 0.01	5.74 ± 0.01	5.36 ± 0.01	5.47 ± 0.03	
$[BMPyrr]^+$		5.43 ± 0.01	5.14 ± 0.01		5.96 ± 0.01

Gardas et al.[24] for imidazolium cations, where the increase of the liquid density does not directly correspond to a rise in the molecular weight of the anion. This can be explained by the stronger localized charge in the thiocyanate anion than in the dicyanamide (two cyanide groups), which gives the possibility of a stronger ion pairing with the pyridinium and imidazolium cation resulting in a higher density.

Cation. The influence of the cation on the density of the RTILs is less obvious compared to that provided by the nature of the anion. The density of the ionic liquid with the same anion does not vary following any common cationic order. Figure 2 shows that for liquids with dicyanamide as anion, the density decreases in the following order: pyrrolidinium > imidazolium > pyridinium. However, for the liquids with thiocyanate as anion, the liquid density decreases as imidazolium > pyridinium > pyrrolidinium. Tokuda et al.[39] found for ionic liquids with bis(trifluoromethane sulfonil)imide anion that density increases as pyrrolidinium < imidazolium < pyridinium. Most likely, the effect of the cation on the density is linked to the kind of atomic associations that a given cation exerts on the counteranion.[41,42]

As expected,[24,44] the density of the R_1-methylimidazolium tetrafluoroborate ionic liquids decreases when the alkyl chain length on the imidazolium cation increases. The effect of the length of the alkyl chain of the imidazolium cation on the molar volume of the ionic liquid is plotted in Figure 3. The positive change in the molar volume by the addition of two $-CH_2$ groups is in average (33.8 ± 0.5) $cm^3 \cdot mol^{-1}$, and that agrees with the values calculated by Gardas et al.[24] [(33.88 ± 0.01) $cm^3 \cdot mol^{-1}$], Gomez de Azevedo[44] (34.56 $cm^3 \cdot mol^{-1}$), and Esperança et al.[43] [(34.4 ± 0.5) $cm^3 \cdot mol^{-1}$].

The thermal expansion evaluates the changes of the liquid volume with temperature. The coefficient of volume expansion at constant pressure or volume expansivity α_p is expressed in eq 4.

$$\alpha_p = -\left(\frac{\partial \ln \rho}{\partial T}\right)_p = \left(\frac{\partial \ln V}{\partial T}\right)_p \tag{4}$$

where V stands for volume, T for temperature, and P for pressure. Other studies[24,45] have found a small variation of the volumetric expansion of the RTILs with temperature. Ambient density measurements show that RTILs have less expansion and are less compressible than regular organic solvents. Besides, RTILs with a longer alkyl chain are more compressible.[46] Given the small variation of the α_p with temperature[24] and simply for a straightforward comparison purpose, it is assumed that α_p is constant.[43] The function of $\ln \rho = f(T)$ is linear, so $\ln V = f(T)$ is also linear, and α_p is a temperature-independent constant. The estimated isobaric volume expansivity α_p constants obtained when plotting $\ln \rho$ versus temperature, eq 4, are reported in Table 4.

The thermal expansion coefficient of the measured RTILs varies between (5.1 and 6.2)$\cdot 10^{-4}$ K^{-1}, which is lower than the thermal expansion coefficient of the traditional solvents. The expansion coefficients of pyridine and butanol are (10.7 and 11.07)$\cdot 10^{-4}$ K^{-1} respectively.[47] The calculated expansivities are similar to those reported by Gu et al.[46] for $[OMIM]BF_4$ and other ionic liquids, which are in the range of (5 to 6)$\cdot 10^{-4}$ K^{-1}. Additionally, the expansivities of $[BMIM]BF_4$ and $[OMIM]BF_4$ are in good agreement with those reported by Harris et al.[21] of (5.9 and 6.2)$\cdot 10^{-4}$ K^{-1}, respectively. For the alkylimidazolium tetrafluoroborate liquids, the α_p decreases as the length of the substitute chain on the cation decreases. Additionally, when comparing the ionic liquids with the same anion and with a butyl and methyl-alkyl chain appended to the cation, the α_p increases as follows: $BMIM^+$ > $BMPy^+$ > $BMPyrr^+$. However, a significant difference of α_p between the two ionic liquids with $MeSO_4^-$ as anion is not observed. Looking at the series of liquids with the same cation, α_p is generally higher when

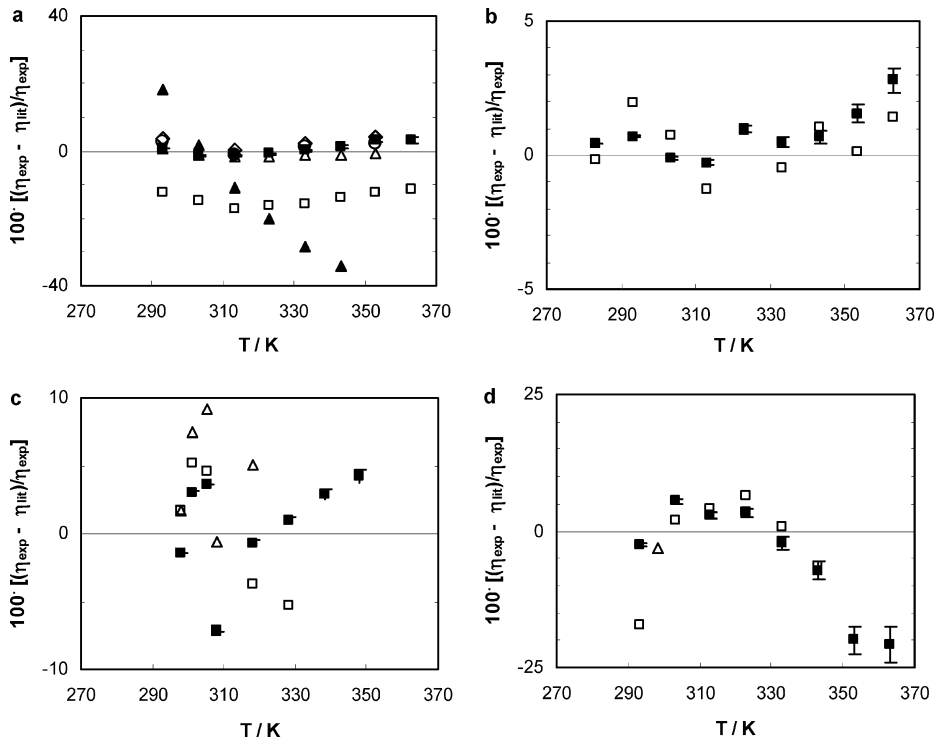


Figure 4. Relative deviation between the experimental viscosity η_{exp} and viscosity data reported in the literature $\eta_{lit.}$ as a function of temperature. ■, This work, deviation of the experimental viscosities of the RTILs from the values obtained using eq 5 and error bars representing the uncertainty. Water mass fraction w is stated where known. (a) $[BMIM]BF_4$ ($w = 100 \cdot 10^{-6}$): ▲, ref 48; □, ref 26 ($w = 307 \cdot 10^{-6}$); △, ref 21 ($w = 77 \cdot 10^{-6}$); ◇, rolling ball viscometer and ○, capillary viscometer from ref 28 ($w = 336 \pm 100 \cdot 10^{-6}$). (b) $[OMIM]BF_4$ ($w = 790 \cdot 10^{-6}$): □, ref 26 ($w = 80 \cdot 10^{-6}$). (c) $[BMPy]BF_4$ ($w = 560 \cdot 10^{-6}$): △, ref 29 ($w = 50 \cdot 10^{-6}$); □, ref 40. (d) [BMIM]DCA ($w = 680 \cdot 10^{-6}$): □, ref 36; △, ref 20 ($w = 256 \cdot 10^{-6}$).

paired to lower molecular weight anions, with the exception of the pyrrolidinium paired with trifluoroacetate.

Viscosity. The measured viscosities are presented in Table 5. The uncertainty in the absolute viscosity η is estimated to be $\pm$ 1 %. The viscosities of [BMIM]BF_4, [OMIM]BF_4, [BMIM]DCA, [BMPy]BF_4, and [BMPy]DCA decrease rapidly when the temperature is increased. The viscosity data were fitted to a Vogel−Fulcher−Tamman (VFT) expression (eq 5).

$$\eta = A' \exp\left[\frac{B'}{T - T_o}\right] \tag{5}$$

The sensitivity analysis of the data shows that from the three fitting parameters (A', B', and T_o) of the VFT equation the viscosity fit is more sensitive to any variation of A'. Table 6 lists the best fit parameters for the VFT relation. Figure 4 shows the relative deviation between the viscosities measured in this

Table 7. Surface Tension γ of the RTILs at T = (293 to 360) K and 0.1 MPa

[BMIM]DCA		[BMPy]DCA		[BMPyrr]DCA		[BMIM]$MeSO_4$	
T/K	$\gamma \pm$ SD / mN·m^{-1}	T/K	$\gamma \pm$ SD / mN·m^{-1}	T/K	$\gamma \pm$ SD / mN·m^{-1}	T/K	$\gamma \pm$ SD / mN·m^{-1}
293.15	48.6 ± 0.3	293.25	43.4 ± 0.3	293.05	56.2 ± 0.1	294.55	42.9 ± 0.2
294.45	48.8 ± 0.3	293.15	43.7 ± 0.1	293.45	56.4 ± 0.2	295.45	43.4 ± 0.3
298.15	48.6 ± 0.1	304.15	42.3 ± 0.1	303.45	55.8 ± 0.2	295.55	43.0 ± 0.1
303.30	48.6 ± 0.1	304.15	42.3 ± 0.1	303.55	55.8 ± 0.2	302.85	42.8 ± 0.2
303.55	48.5 ± 0.2	312.15	39.1 ± 0.2	312.45	54.8 ± 0.1	302.75	42.7 ± 0.2
316.15	47.2 ± 0.1	314.05	42.0 ± 0.2	312.45	54.0 ± 0.1	310.65	42.5 ± 0.3
325.15	46.3 ± 0.1	314.05	42.0 ± 0.1	322.15	53.8 ± 0.2	309.65	44.1 ± 0.3
344.15	45.0 ± 0.1	322.95	40.7 ± 0.2	322.35	53.7 ± 0.1	309.75	42.4 ± 0 0.2
332.05	45.7 ± 0.3	322.35	39.4 ± 0.1	332.15	53.1 ± 0.1	310.15	42.3 ± 0.1
332.85	45.5 ± 0.1	330.25	39.0 ± 0.1	331.95	53.3 ± 0.1	321.55	41.9 ± 0.3
341.15	45.8 ± 0.1	331.15	38.4 ± 0.1	342.55	51.6 ± 0.1	320.45	41.7 ± 0.1
344.15	45.0 ± 0.1	340.35	38.5 ± 0.1	342.65	51.6 ± 0.1	331.55	41.0 ± 0.2
		340.45	38.3 ± 0.2	352.85	50.8 ± 0.1	331.55	41.3 ± 0.1
		340.75	38.7 ± 0.2	352.95	51.1 ± 0.1	331.45	41.3 ± 0.1
		341.55	37.6 ± 0.1	353.45	51.2 ± 0.2	340.35	41.5 ± 0.2
		342.35	37.2 ± 0.1			340.45	40.7 ± 0.1
		349.95	36.8 ± 0.2			342.65	38.7 ± 0.1
		350.45	36.3 ± 0.1			342.35	38.1 ± 0.1
						353.75	38.2 ± 0.1
						353.15	38.0 ± 0.2
						354.35	37.7 ± 0.1

[BMIM]BF_4		[OMIM]BF_4		[BMPy]BF_4		[BMPyrr]TFA	
T/K	$\gamma \pm$ SD / mN·m^{-1}	T/K	$\gamma \pm$ SD / mN·m^{-1}	T/K	$\gamma \pm$ SD / mN·m^{-1}	T/K	$\gamma \pm$ SD / mN·m^{-1}
293.65	44.6 ± 0.2	298.45	32.3 ± 0.3	291.15	45.1 ± 0.1	292.05	35.7 ± 0.1
303.35	43.8 ± 0.3	303.35	32.0 ± 0.1	294.25	44.6 ± 0.2	292.15	35.7 ± 0.1
312.85	43.3 ± 0.1	313.15	31.6 ± 0.3	298.65	45.1 ± 0.1	294.05	35.9 ± 0.3
312.95	43.2 ± 0.4	323.05	30.9 ± 0.3	300.15	45.2 ± 0.2	294.45	35.8 ± 0.3
322.55	42.5 ± 0.3	332.85	30.4 ± 0.3	304.05	44.6 ± 0.1	307.35	34.9 ± 0.1
322.65	42.5 ± 0.2	343.15	29.7 ± 0.4	303.95	44.7 ± 0.1	307.15	35.0 ± 0.1
332.25	42.1 ± 0.2	352.95	29.1 ± 0.4	314.15	44.5 ± 0.3	309.15	35.3 ± 0.2
341.95	42.0 ± 0.3	361.85	28.7 ± 0.3	311.85	44.6 ± 0.3	310.15	34.9 ± 0.1
351.55	41.0 ± 0.1			311.85	44.2 ± 0.1	311.65	35.3 ± 0.2
360.95	40.3 ± 0.2			320.25	43.7 ± 0.1	312.45	34.8 ± 0.1
				322.05	43.6 ± 0.1	320.15	34.4 ± 0.1
				331.55	43.0 ± 0.1	320.25	34.2 ± 0.1
				330.95	43.1 ± 0.2	330.15	34.2 ± 0.2
				341.75	42.7 ± 0.2	330.25	34.2 ± 0.2
				342.45	42.3 ± 0.1	341.85	34.2 ± 0.3
				350.75	42.5 ± 0.4	357.05	33.4 ± 0.2
						357.55	33.3 ± 0.1

[BMIM]SCN		[BMPy]SCN		[BMPyrr]SCN	
T/K	$\gamma \pm$ SD / mN·m^{-1}	T/K	$\gamma \pm$ SD / mN·m^{-1}	T/K	$\gamma \pm$ SD / mN·m^{-1}
295.85	46.9 ± 0.1	302.85	47.7 ± 0.1	303.35	49.8 ± 0.1
292.35	47.3 ± 0.3	302.95	47.6 ± 0.1	312.15	47.4 ± 0.2
293.65	47.0 ± 0.2	312.35	45.2 ± 0.1	312.35	47.3 ± 0.1
303.45	46.1 ± 0.2	312.85	45.8 ± 0.1	322.15	48.4 ± 0.2
303.35	45.9 ± 0.2	320.15	45.8 ± 0.1	322.15	48.3 ± 0.1
326.25	39.5 ± 0.2	320.35	46.0 ± 0.1	322.65	48.0 ± 0.1
330.55	40.0 ± 0.2	330.15	39.5 ± 0.1	322.95	48.0 ± 0.1
334.95	36.5 ± 0.1	330.75	40.9 ± 0.1	330.85	47.6 ± 0.1
349.35	36.9 ± 0.2	341.75	36.1 ± 0.2	311.85	45.4 ± 0.2
350.85	36.6 ± 0.1	341.95	40.7 ± 0.3	311.55	45.6 ± 0.2
		342.15	38.4 ± 0.1	340.55	44.7 ± 0.2
				341.35	42.1 ± 0.3
				341.65	45.3 ± 0.2
				343.45	44.5 ± 0.3
				344.15	44.7 ± 0.1

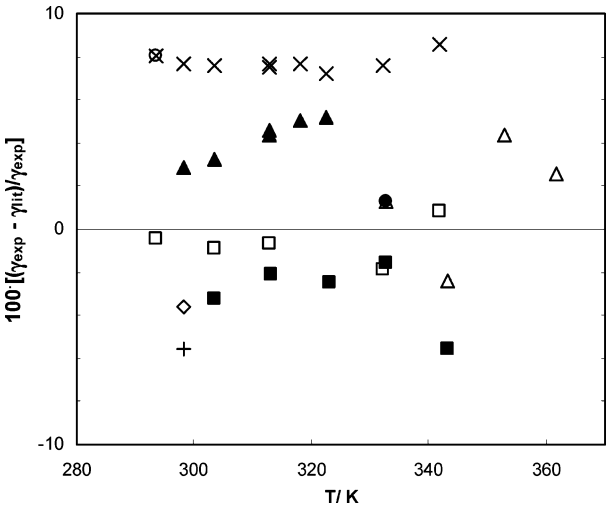


Figure 5. Relative deviation between the experimental surface tension γ_{exp} and viscosity data reported in the literature $\gamma_{lit.}$ as a function of temperature. Water mass fraction w is stated where known. Symbols: □, [BMIM]BF_4, ref 31 ($w = 485 \cdot 10^{-6}$); ▲, [BMIM]BF_4 ref 32 ($w = 200 \cdot 10^{-6}$); ○, [BMIM]BF_4, ref 33; ×, [BMIM]BF_4, ref 34; ◇, [BMIM]BF_4, ref 30; +, [BMIM]BF_4, ref 49; ■, [OMIM]BF_4, ref 31 ($w = 371 \cdot 10^{-6}$); △, [OMIM]BF_4, ref 34; ●, [OMIM]BF_4, ref 33.

Table 8. Surface Thermodynamic Functions H^A (Equation 6) and S_o (Equation 7) of the RTILs

RTIL	$10^3 \cdot S_o$/J·m^{-2}·K^{-1}	$10^3 \cdot H^A$/J·m^{-2}
[BMIM]BF_4	0.0593 ± 0.003	61.80 ± 0.04
[OMIM]BF_4	0.0581 ± 0.003	49.67 ± 0.09
[BMPy]BF_4	0.0607 ± 0.008	63.10 ± 0.01
[BMIM]DCA	0.0775 ± 0.003	71.88 ± 0.28
[BMPy]DCA	0.1181 ± 0.012	78.10 ± 0.03
[BMPyrr]DCA	0.0897 ± 0.004	82.84 ± 0.20
[BMIM]SCN	0.2023 ± 0.010	106.11 ± 1.53
[BMPy]SCN	0.2219 ± 0.022	114.92 ± 0.12
[BMPyrr]SCN	0.0995 ± 0.015	79.41 ± 0.77
[BMIM]$MeSO_4$	0.0874 ± 0.004	69.36 ± 0.25
[BMPyrr]TFA	0.0370 ± 0.002	46.31 ± 0.28

study and those found in the literature as a function of temperature. The viscosity of [BMIM]BF_4 deviates up to (35 and 16) % from those reported by Okoturo et al.[48] and Seddon et al.[26] But when the viscosity of [BMIM]BF_4 is compared with the data reported by Harris et al.[21] and Tomida et al.,[28] the relative deviations are smaller than 4 %. As expected, given the higher water content of our [BMIM]BF_4 sample, the measured viscosity is smaller than that of Harris et al.[21] with a relative deviation of (0.5 to 1.5) %. The measured viscosity of [OMIM]BF_4 deviates only 1.5 % from the data from Seddon et al.,[26] although the water content of our sample is about ten times higher than the one reported by Seddon. The viscosity of [BMPy][BF_4] is higher than those reported by Khupse et al.[29] and Bandres et al.[40] with maximum relative deviations of (10 and 7) %, respectively. The relative deviation between the experimental viscosities of [BMIM]DCA and the values obtained with eq 5 are higher lower than 10 % between (298 and 353) K and higher than 10 % from > 353 K. At the temperature range from (298 to 343) K, the deviations between our [BMIM]DCA data and the viscosities reported by Yoshida et al.[36] and McHale et al.[20] are lower than 6 %. However, at 293 K the difference between our data and the value reported by Yoshida is 17 %.

The measured viscosities were higher for the liquids with pyridinium cation than those obtained for the imidazolium-based liquids. As anticipated,[36] the increase of the length of the substituted alkyl chain in the imidazolium cation, from butyl to octyl, when paired with tetrafluoroborate produced an increase in the viscosity.

Surface Tension. The measured surface tension data are reported in Table 7. The uncertainty of the surface tension measurements is ± 0.2 mN·m^{-1}. The selected RTILs have a surface tension lower than that of water and larger than most of the common organic solvents. At 293 K, the surface tensions of water,[51,52] acetone,[47] and methanol[47] are (72.7, 23.7, and 22.6) mN·m^{-1}. Through the whole range of measured temperatures, [BMPyrr]DCA exhibits the highest surface tension, while the lowest was measured for [BMPyrr]TFA. The surface tensions at 293 K of [BMPyrr]DCA and [BMPyrr]TFA are (56.2 and 35.7) mN·m^{-1}, respectively.

As observed before,[31−35] the surface tension of the measured RTILs decreases with a rise in temperature. The relative deviations between the experimental surface tension and those reported in the literature are presented in Figure 5. The surface tensions reported by Freire et al.[31] for [BMIM]BF_4 are slightly higher than the data measured here, despite the fact that the water content of the sample used by them was higher than the water content of our [BMIM]BF_4 sample. On the other hand, the surface tensions of [OMIM]BF_4 reported by Freire et al.[31] are also higher than our data, while the water content of our sample was higher than the one reported by Freire. The deviations between our measurements for [BMIM]BF_4 and [OMIM]BF_4 and the data reported by Freire et al.[31] are in average (0.6 and 3) %, respectively. The surface tensions reported by Law et al.[33,34] and Kim et al.[32] for [BMIM]BF_4 are lower than those measured in this study with average deviations of (8 and 4) %, respectively. The deviation between the our measurements and the data reported by Law et al.[33,34] for [OMIM]BF_4 is in average 1.5 %.

The surface energy enthalpy H^A and surface energy entropy S_o can be estimated based on the measured surface tension at atmospheric pressure. The surface thermodynamic functions are derived from the temperature dependence of the surface tension measurements,[53] according to eq 6 and eq 7.

$$\gamma = H^A - T \cdot S_o \tag{6}$$

$$S_o = -\left(\frac{\partial \gamma}{\partial T}\right)_p \tag{7}$$

The surface excess entropy and calculated enthalpy are presented in Table 8. The surface entropies of the RTILs are low, which gives an indication of the high level of organization of the ionic liquid structure.[54] The estimated surface entropies of ethanol, water, benzene, and pyridine are (0.086, 0,138, 0.13, and 0.1369)·10^{-3} J·m^{-2}·K^{-1}, respectively.[47]

Effect of the Variation of Anion and Cation on the RTIL Surface Tension. Anion. The results indicate that both cation and anion have an effect on the surface tension of the ionic liquids. The surface tension corresponds to the part of the molecule that is present at the interface.[31,34,54] Both anion and cation are present at the liquid surface and should therefore both contribute to the surface free energy.[33,34] Freire et al.[31] proposed that mostly energetic interactions determine the surface tension, as the rise in the anion size and the rising of the diffuse nature of the anion negative charge lead to a more delocalized charge and consequently to a decrease on the ability to hydrogen bond. However, contrary to that stated by Freire, in our results an increase in the anion size was not directly associated with a reduction in the surface tension.

At higher temperatures, the surface tension of the imidazolium-based ionic liquids increases as follows: $SCN^- < MeSO_4^- < BF_4^- < DCA^-$. For the pyridinium-based liquids, the surface

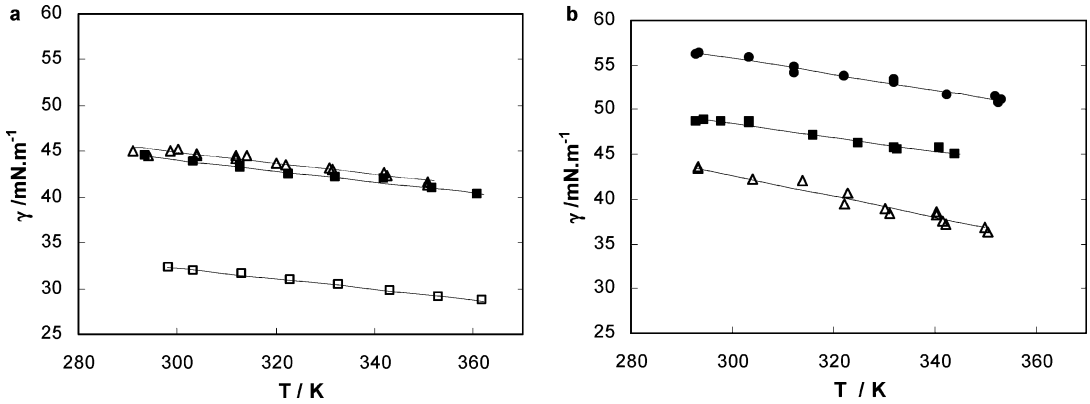


Figure 6. Cation effect on the surface tension of the RTILs γ as a function of temperature. (a) BF_4^--based RTILs: ■, $[BMIM]BF_4$; □, $[OMIM]BF_4$; △, $[BMPy]BF_4$. (b) DCA^--based RTILs: ■, [BMIM]DCA; △, [BMPy]DCA; ●, [BMPyrr]DCA. Lines plotted as a view aid.

tension of the tetrafluoroborate anion is higher than that of the liquid with the dicyanamide anion, for the whole range of temperatures (see Figure 6). Within the ionic liquids with imidazolium and pyridinium cations, the highest entropy was calculated for the liquids with thiocyanate as the anion, and the lowest entropy was calculated for the liquids in which the anion was tetrafluoroborate.

The surface tension of the ionic liquid with pyrrolidinium as cation increases following the next anion order: $TFA^- < SCN^- < DCA^-$. Likewise, for the pyrrolidinium-containing group, the highest entropy was exhibited by the liquids with thiocyanate as anion, and the smallest surface excess entropy is observed in the liquid paired with trifluoroacetate. The surface tension increases as the molar volume of the liquids with the pyrrolidinium cation decreases.

The highest surface enthalpy was observed for the liquids with thiocyanate as anion and the lowest for the liquids with fluorine-containing anions. As well as observed by Law et al.,[34] and proposed by Freire at al.,[31] the liquids containing fluorinate ions, as trifluoroacetate, exhibited a low surface tension.

Cation. Figure 6 shows that the surface tension of the $[BMPy]BF_4$ is slightly higher that the surface tension of $[BMIM]BF_4$. Besides, the increment on the length of the alkyl chain of the imidazolium cation produces a reduction on the surface tension since the surface tension of $[BMIM]BF_4$ is higher than the surface of $[OMIM]BF_4$. The decrease in the surface tension coincides with the increase of the molar volume of the alkyl-imidazolium tetrafluoroborate liquids. The increase in the size of the molecule leads to an increase of the van der Waals forces[31,34] and also contributes to the dispersion of the ion charge and therefore to a decrease on the hydrogen bond strength.[31] The surface enthalpy decreases when the butyl is replaced with an octyl chain. In addition, for some imidazolium-based ionic liquids, the surface properties are influenced by the surface orientation and structure of the cation.[34,55] For the ionic liquids with dicyanamide as anion, the surface tension decreases as $[BMPyrr]^+ > [BMIM]^+ > [BMPy]^+$. In the liquids with thiocyanate as anion, the surface tension decreases in the next order: $[BMPyrr]^+ > [BMPy]^+ > [BMIM]^+$. Moreover, for the series of ionic liquids with a similar anion, those paired with pyridiniun exhibited the highest entropy.

Conclusions

Experimental density, viscosity, and surface tension data of 13 pure ionic liquids in the temperature range from (293 to 263) K and at 0.1 MPa are reported. For all the studied RTILs, the density, viscosity, and surface tension decrease when temperature increases. The density measurements of RTILs were linearly correlated and used to estimate expansivity coefficients α_p. The measured viscosities were correlated with a Vogel−Fulcher−Tamman equation with average deviations from the experimental viscosity data lower than 5 %. The surface thermodynamic properties of excess energy H^A and entropy S_o were estimated from the measured surface tension data sets. From the experimental results, it is clear that both the nature of the forming ions and also the type of possible interactions between anion and cation determine the ionic liquid properties.

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