JOURNAL OF
CHEMICAL &
ENGINEERING
DATA

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pubs.acs.org/jced

Thermophysical Properties of 1-Ethyl-3-methylimidazolium 1,1,2,2-Tetrafluoroethanesulfonate and 1-Ethyl-3-methylimidazolium Ethylsulfate Ionic Liquids as a Function of Temperature

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ABSTRACT: Refractive indices, densities, and viscosities of 1-ethyl-3-methylimidazolium 1,1,2,2-tetrafluoroethanesulfonate ([emim][$CHF_2CF_2SO_3$]), and 1-ethyl-3-methylimidazolium ethylsulfate ([emim][$CH_3CH_2SO_4$]) ionic liquids (ILs) were measured over the temperature range from (293.15 to 353.15) K at atmospheric pressure. The surface tension of the two ILs was also determined at temperatures between (303.15 and 333.15) K. The reliability of the results gathered in this work was assessed by comparing experimental values of [emim][$CH_3CH_2SO_4$] with data available in the literature. Molar volumes, molar refractions, molar free volumes, volume expansivities, surface entropies, surface enthalpies, and critical temperatures of the ILs were calculated from the experimental data. The influence of temperature on the viscosity was described by the Arrhenius and Vogel−Fulcher−Tammann (VFT) models. The variation of surface tension with temperature was modeled using the Eötvös equation. An evaluation of the influence of several sulfur and fluorinated anions on the physical properties of 1-ethyl-3-methylimidazolium based-ILs was performed by comparison between experimental measurements of [emim][$CHF_2CF_2SO_3$] and [emim][$CH_3CH_2SO_4$] and published data of 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([emim][CF_3SO_3]) and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([emim][$(CF_3SO_2)_2N$]).

INTRODUCTION

An ionic liquid (IL) is a salt composed entirely of ions with a melting temperature below 373 K.[1] During the past decade, the number of IL publications follows an exponential growth curve.[2] This growing interest in ILs is due to their singular physicochemical properties. The most remarkable feature of ILs is their practically negligible vapor pressure, although some ILs can be distilled under vacuum without decomposition.[3] As a result of this exceptional property, the ILs can be used to replace the volatile organic compounds (VOCs) in many chemical processes.[4] Thereby, the application of ILs would prevent the environmental pollution caused by emission of VOCs.[1]

In addition to the environmental benefit, ILs have other advantages over conventional solvents from a technical point of view. These compounds have a wide liquid temperature range, in some cases greater than 400 K,[5] and their physicochemical properties can be tuned by changing the structure of the anion, the cation, or both. Hence, the ILs can be considered as designer solvents.[6] The presence of impurities, such as chloride and water, significantly affects the physical properties of ILs.[5] Therefore, the physical properties measurements must be always accompanied by the specification of the IL.[1] In order to make a proper design of the chemical processing and reaction units, it is essential to determine accurately the thermophysical properties of ILs.[7] Considering the large number of cation−anion combinations, it is difficult to obtain the physical properties of all synthesized ILs. Thus, it is necessary to study the relationships between ionic structure and properties to implement predictive models.[8,9]

The aim of this study was to determine refractive index, density, viscosity, and surface tension of 1-ethyl-3-methylimidazolium 1,1,2,2-tetrafluoroethanesulfonate ([emim][$CHF_2CF_2SO_3$]) and 1-ethyl-3-methylimidazolium ethylsulfate ([emim][$CH_3CH_2SO_4$]) ILs as a function of temperature at atmospheric pressure. The validation of the obtained results was performed by using physical properties of the [emim][$CH_3CH_2SO_4$] from the literature.[8,10−17] The influence of temperature on the physical properties was studied and fitted to appropriate models. Comparisons with published data of 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([emim][CF_3SO_3]) and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([emim][$(CF_3SO_2)_2N$]) were made to study the effect of the anion structure on the physical properties of 1-ethyl-3-methylimidazolium based-ILs. These ILs have been selected because they are formed by sulfur and fluorinated anions as the ILs used in this work.

EXPERIMENTAL SECTION

Chemicals. [emim][$CHF_2CF_2SO_3$] and [emim][$CH_3CH_2SO_4$] ILs were purchased from Iolitec GmbH, with nominal mass fraction purity greater than 0.99 and water and halides mass fractions lower than 0.0001. Water content and purity of the ILs were measured by the manufacturer using Karl Fisher titration and NMR analysis, respectively. The physical properties of the ILs were measured as received, without further purification. During the experimental period, they were stored in their original vessels in a desiccator to maintain constant water content. The handling of ILs was carried out under a dry nitrogen atmosphere, inside a glovebox.

Refractive Index. Refractive indices were measured from 293.15 K to 353.15 K (± 0.1 K) using a Rudolph Research

Received: May 6, 2011
Accepted: August 6, 2011
Published: August 22, 2011

Table 1. Refractive Index (n_D), Density (ρ), Dynamic Viscosity (η), and Surface Tension (γ) of [emim][$CHF_2CF_2SO_3$] and [emim][$CH_3CH_2SO_4$] ILs as a Function of Temperature

T/K	n_D	ρ/ g·cm^{-3}	η/ mPa·s	$10^3\gamma$/ N·m^{-1}
		[emim][$CHF_2CF_2SO_3$]		
293.15	1.44100	1.43584	117.43	
303.15	1.43833	1.42744	72.64	43.29
313.15	1.43570	1.41904	48.32	42.45
323.15	1.43304	1.41067	33.94	42.03
333.15	1.43041	1.40233	25.05	41.43
343.15	1.42777	1.39402	18.86	
353.15	1.42514	1.38576	14.74	
		[emim][$CH_3CH_2SO_4$]		
293.15	1.47959	1.24186	122.07	
303.15	1.47694	1.23506	75.10	47.34
313.15	1.47429	1.22828	49.84	46.67
323.15	1.47158	1.22154	35.34	46.17
333.15	1.46893	1.21484	25.93	45.53
343.15	1.46625	1.20819	19.36	
353.15	1.46359	1.20158	15.12	

Analytical J357 refractometer. The optical wavelength utilized was 589.3 nm (Na-D line). Millipore quality water was used for calibration of the apparatus before all measurements. The repeatability was lower than $\pm 4 \cdot 10^{-5}$, and the uncertainty in refractive index measurements was estimated to be less than $\pm 9 \cdot 10^{-5}$.

Density. Density measurements were performed using an Anton Paar DMA-5000 oscillating U-tube density meter. The effect of the viscosity on density determination was automatically corrected by a factor depending on the viscosity of the sample. Densities of [emim][$CHF_2CF_2SO_3$] and [emim][$CH_3CH_2SO_4$] ILs were measured in the temperature range from 293.15 K to 353.15 K (± 0.01 K) at atmospheric pressure. Prior to each measurement, density measurements of Millipore quality water were made in order to check the calibration of the densimeter. The repeatability and the uncertainty in measurements were estimated to be less than $\pm 1 \cdot 10^{-6}$ g·cm^{-3} and $\pm 1 \cdot 10^{-5}$ g·cm^{-3}, respectively.

Dynamic Viscosity. Dynamic viscosities of [emim][$CHF_2CF_2SO_3$] and [emim][$CH_3CH_2SO_4$] were determined over temperature range from 293.15 K to 353.15 K using an Anton Paar Automated Micro Viscometer (AMVn). The temperature was controlled by a Pt100 temperature sensor with a resolution of ± 0.01 K. The measurement method of this instrument was the falling ball principle. It consists of the determination of the ball's rolling time in a calibrated glass capillary filled with sample. The calibration of the capillary was performed by the manufacturer using viscosity standard fluids. The estimated experimental uncertainty was estimated to be less than ± 0.5 %, and the repeatability was less than ± 0.1 %.

Surface Tension. A Dataphysics OCA 15 plus tensiometer was used for measurement of surface tensions of [emim][$CHF_2CF_2SO_3$] and [emim][$CH_3CH_2SO_4$] ILs at temperature range from 303.15 K to 333.15 K. A pendant drop of the IL was formed inside a thermostatted chamber heated using a Julabo F12-EC bath. The chamber temperature was measured by a Pt100 probe with a precision of ± 0.1 K. The drop shape was determined by a charge-coupled device (CCD) video camera and the surface tension was calculated by the software SCA 20 OCA using the Young−Laplace equation. Measurements of the surface tension of Millipore quality water were performed in order to check the validity of the measurement method. The uncertainty of the measurements was estimated less than ± 0.05 mN·m^{-1}.

RESULTS AND DISCUSSION

The refractive index (n_D), the density (ρ), the dynamic viscosity (η), and the surface tension (γ) of [emim][$CHF_2CF_2SO_3$] and [emim][$CH_3CH_2SO_4$] ILs were determined as a function of temperature at intervals of 10 K and atmospheric pressure. The experimental values of these physical properties are summarized in Table 1. The refractive indices, densities, and viscosities values are the average of three independent measurements, whereas the surface tension reported data are the average of ten determinations.

Refractive Index. The refractive index values of [emim][$CHF_2CF_2SO_3$] and [emim][$CH_3CH_2SO_4$] against temperature are shown in Figure 1. As expected, refractive indices of the two ILs decrease with temperature. A proper fit was achieved using the following linear temperature equation

$$n_D = a + b \cdot T \tag{1}$$

where n_D denotes the refractive index of the IL, a and b are fitting parameters, and T is the measured temperature in K. Adjustable parameters and correlation coefficients (R^2) are presented in Table 2. The values calculated using this linear regression model are plotted as solid lines in Figure 1 along with experimental data.

Molar volumes were calculated from experimental densities as the ratio between molecular weight and density of each IL. Molar refractions of the two ILs were estimated using the Lorentz−Lorenz formula[18]

$$R_m = \left(\frac{{n_D}^2 - 1}{{n_D}^2 + 2}\right) V_m \tag{2}$$

where V_m is the molar volume and n_D denotes the refractive index of the IL. Calculated molar refractions and molar volumes of [emim][$CHF_2CF_2SO_3$] and [emim][$CH_3CH_2SO_4$] as a function of temperature are listed in Table 3.

Several authors defend that refractive index depends on molar free volume $V_{m,f}$, which is the unoccupied fraction of the molar volume of an IL.[10,18−20] Increasing the molar free volume decreases the refractive index. Molar free volume ($V_{m,f}$) of a substance can be estimated as follows:

$$V_{m,f} = V_m - R_m \tag{3}$$

where V_m is the molar volume and R_m indicates the molar refraction of the IL estimated with eq 2. The calculated molar free volumes are also shown in Table 3. The free molar volume of [emim][$CHF_2CF_2SO_3$] is higher than that of [emim][$CH_3CH_2SO_4$] at the temperature range studied. This fact explains why the refractive index of [emim][$CHF_2CF_2SO_3$] is quite lower than that of [emim][$CH_3CH_2SO_4$], and it shows the influence of anion structure on refractive index.

In order to validate the experimental method of measuring refractive index, measured refractive indices of the [emim][$CH_3CH_2SO_4$] were compared with literature data for the same IL.[11] The differences between the experimental refractive indices and those reported by Gómez et al. were less than 0.08 %.[11] Thus, the measuring procedure can be considered as a sufficiently accurate method and the results for both ILs can be validated.

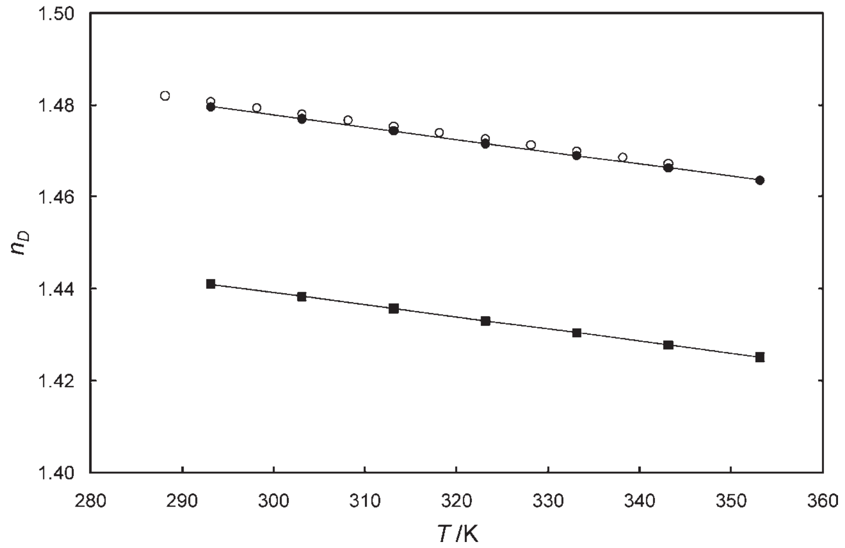

Figure 1. Refractive indices as a function of temperature: ■, Experimental data of [emim][$CHF_2CF_2SO_3$]; ●, Experimental data of [emim][$CH_3CH_2SO_4$]; ○, [emim][$CH_3CH_2SO_4$] (from ref 11). Solid line indicates calculated values by the linear fit of the experimental data.

Table 2. Fitting Parameters (a and b) and Correlation Coefficient (R^2) of eq 1 for the Refractive Indices of [emim][$CHF_2CF_2SO_3$] and [emim][$CH_3CH_2SO_4$] ILs

a	b	R^2
	[emim][$CHF_2CF_2SO_3$]	
1.51844	-2.64×10^{-4}	0.99999
	[emim][$CH_3CH_2SO_4$]	
1.55785	-2.67×10^{-4}	0.99999

Density. Experimental densities of [emim][$CHF_2CF_2SO_3$] and [emim][$CH_3CH_2SO_4$] as a function of temperature are shown in Figure 2. In order to analyze the influence of the anion on the density of 1-ethyl-3-methylimidazolium based-ILs, literature density data for [emim][CF_3SO_3][12] and [emim][($CF_3SO_2)_2N$][21] are also plotted.

The density of [emim][$CHF_2CF_2SO_3$] is higher than that of [emim][$CH_3CH_2SO_4$] at all temperatures studied. This trend can be explained by the higher molecular weight of the 1,1,2,2-tetrafluoroethanesulfonate anion. The influence of the molecular weight of the anion on the densities of imidazolium-based ILs has been widely studied.[10,20,22] In these works, the authors report that the density of an IL increases with molecular weight of the anion, as occurs in our experimental data. Hence, the densities of [emim][($CF_3SO_2)_2N$][21] are higher than the published data for [emim][CF_3SO_3][12] and our experimental values for [emim][$CHF_2CF_2SO_3$] and [emim][$CH_3CH_2SO_4$], because these three ILs have a lower anion molecular weight. Seki et al. have also analyzed the dependence of the density on the number of fluorine atoms in the anion.[23] As a result of the high atomic weight of fluorine, the presence of fluorine atoms leads to an increase in the density.

As shown in Figure 2, density seems to decrease linearly with increasing temperature, but several authors have used a second-order polynomial equation to fit the density data of ILs.[10,12,20]

Table 3. Calculated Molar Volumes (V_m), Molar Refractions (R_m), and Molar Free Volumes ($V_{m,f}$) of [emim][$CHF_2CF_2SO_3$] and [emim][$CH_3CH_2SO_4$] at Several Temperatures

T/K	V_m/ $cm^3 \cdot mol^{-1}$	R_m/ $cm^3 \cdot mol^{-1}$	$V_{m,f}$/ $cm^3 \cdot mol^{-1}$
		[emim][$CHF_2CF_2SO_3$]	
293.15	203.54	53.75	149.79
303.15	204.74	53.78	150.96
313.15	205.95	53.82	152.13
323.15	207.17	53.85	153.32
333.15	208.40	53.88	154.52
343.15	209.65	53.91	155.74
353.15	210.90	53.94	156.96
		[emim][$CH_3CH_2SO_4$]	
293.15	190.27	54.01	136.26
303.15	191.32	54.05	137.27
313.15	192.37	54.09	138.28
323.15	193.44	54.12	139.32
333.15	194.50	54.16	140.34
343.15	195.57	54.19	141.38
353.15	196.65	54.22	142.43

In this work, the experimental densities were fitted using the following temperature functions:

$$\rho = a + bT \tag{4}$$

$$\rho = k_0 + k_1 T + k_2 T^2 \tag{5}$$

where T is the measured temperature in K, a and b are the linear fit coefficients, and k_0, k_1, and k_2 are fitting parameters of the quadratic polynomial model. Adjustable parameters of the fits are listed in Table 4. In order to select the most appropriate model for fitting to the experimental data, we have performed an

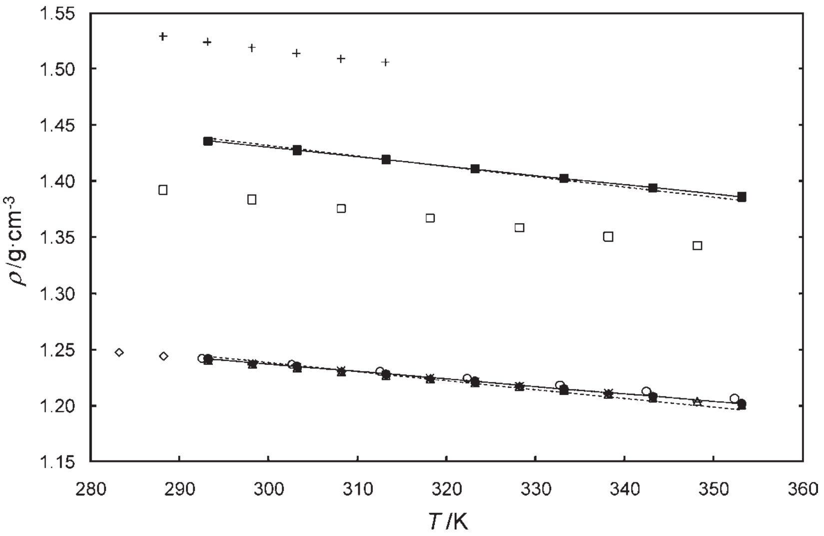

Figure 2. Plot of values of densities against temperature: ■, experimental data of [emim][$CHF_2CF_2SO_3$]; ●, experimental data of [emim][$CH_3CH_2SO_4$]; Δ, [emim][$CH_3CH_2SO_4$] (from ref 13); ◇, [emim][$CH_3CH_2SO_4$] (from ref 14); ○, [emim][$CH_3CH_2SO_4$] (from ref 8); *, [emim][$CH_3CH_2SO_4$] (from ref 11); –, [emim][$CH_3CH_2SO_4$] (from ref 12); -, [emim][$CH_3CH_2SO_4$] (from ref 15); □, [emim][CF_3SO_3] (from ref 12); +, [emim][$(CF_3SO_2)_2N$] (from ref 21). Solid lines represent quadratic polynomial fits of the experimental densities. Dashed lines denote the estimated densities by using eq 8.

Table 4. Adjustable Parameters of Linear and Quadratic Polynomial Fits for the Density of [emim][$CHF_2CF_2SO_3$] and [emim][$CH_3CH_2SO_4$] ILs

linear fit				second-order polynomial fit				
a/ g·cm^{-3}	b/ g·cm^{-3}·K^{-1}	R^2	s/ g·cm^{-3}	k_2/ g·cm^{-3}·K^{-2}	k_1/ g·cm^{-3}·K^{-1}	k_0/ g·cm^{-3}	R^2	s/ g·cm^{-3}
				[emim][$CHF_2CF_2SO_3$]				
1.68059	-8.35×10^{-4}	0.99999	$6 \cdot 10^{-5}$	$1.46 \cdot 10^{-7}$	$-9.29 \cdot 10^{-4}$	1.69572	0.99999	$1 \cdot 10^{-5}$
				[emim][$CH_3CH_2SO_4$]				
1.43859	-6.71×10^{-4}	0.99997	$9 \cdot 10^{-5}$	$1.99 \cdot 10^{-7}$	$-8.00 \cdot 10^{-4}$	1.45930	0.99999	$1 \cdot 10^{-5}$

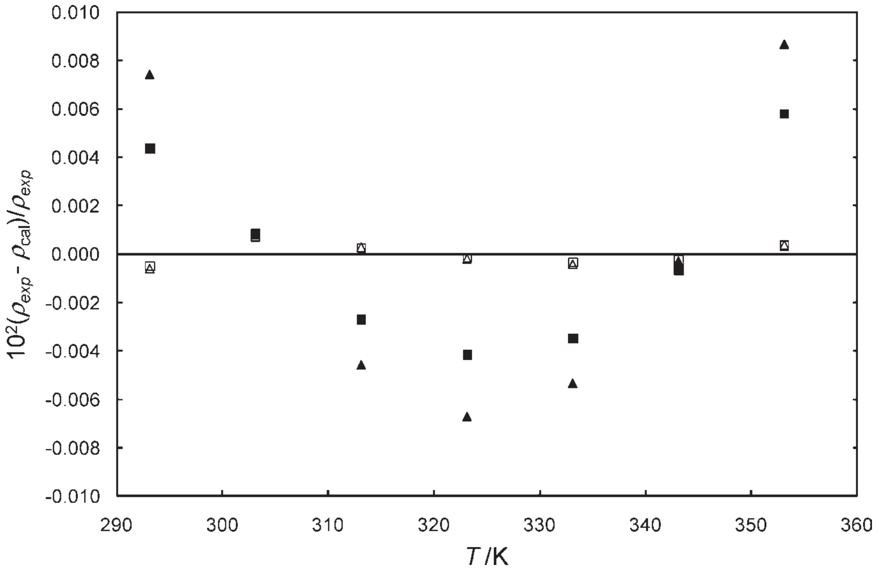

Figure 3. Deviations between experimental and predicted densities as a function of temperature: ■, linear fit for [emim][$CHF_2CF_2SO_3$]; ▲, linear fit for [emim][$CH_3CH_2SO_4$]; □, quadratic polynomial fit for [emim][$CHF_2CF_2SO_3$]; Δ, quadratic polynomial fit for [emim][$CH_3CH_2SO_4$].

Table 5. Estimation of Volume Expansivities (α) of [emim][$CHF_2CF_2SO_3$] and [emim][$CH_3CH_2SO_4$] from Density Measurements

	$10^4\alpha/K^{-1}$	
T/K	[emim][$CHF_2CF_2SO_3$]	[emim][$CH_3CH_2SO_4$]
293.15	5.85 ± 0.06	5.48 ± 0.08
303.15	5.88 ± 0.07	5.50 ± 0.08
313.15	5.91 ± 0.07	5.50 ± 0.08
323.15	5.93 ± 0.07	5.50 ± 0.08
333.15	5.93 ± 0.07	5.49 ± 0.08
343.15	5.94 ± 0.07	5.49 ± 0.08
353.15	5.96 ± 0.07	5.49 ± 0.08

analysis of the residuals and we have calculated the standard deviation of the fits as follows:

$$s = \left[\sum_{i}^{N}\left(\frac{\rho_{\text{exp}} - \rho_{\text{cal}}}{\rho_{\text{exp}}}\right)^2 / (n_d - n_p)\right]^{0.5} \tag{6}$$

where ρ_{exp} is the experimental density, ρ_{cal} denotes the calculated density at each temperature, and n_d and n_p are the number of experimental data and the number of parameters of the corresponding equation, respectively.

The differences between experimental and calculated density data are represented in Figure 3. As can be expected, the second-order polynomial fit provides a lower standard deviation than the linear model. Moreover, the residuals from both models are less than 0.01 %. However, the residuals from linear regression present a slight curvature, which demonstrates that the densities of [emim][$CH_3CH_2SO_4$] and [emim][$CHF_2CF_2SO_3$] do not decrease linearly with temperature. Therefore, the quadratic polynomial model provides a better fit. This nonlinear behavior of the density was observed by Rodríguez et al. for the following 1-ethyl-3-methylimidazolium-based ILs: [emim][$CH_3CH_2SO_4$], [emim][CF_3SO_3], and 1-ethyl-3-methylimidazolium trifluoroacetate ([emim][TFA]).[12]

From experimental density data, the volume expansivities of the ILs (α), also called thermal expansion coefficients, were calculated as follows:[13]

$$\alpha = \frac{1}{V_m}\left(\frac{\partial V_m}{\partial T}\right)_p = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_p \tag{7}$$

where V_m is the molar volume of the compound and the subscript "p" denotes constant pressure. The volume expansivities of the [emim][$CHF_2CF_2SO_3$] and the [emim][$CH_3CH_2SO_4$] at experimental temperatures are listed in Table 5. As seen, the volume expansivity of [emim][$CHF_2CF_2SO_3$] increases with increasing temperature. This is the usual behavior in ILs and in most fluids. However, the volume expansivity of [emim][$CH_3CH_2SO_4$] is almost constant with temperature and even decreases slightly at higher temperatures. Volume expansivity of a substance must tend to infinity as the critical temperature approaches; hence, there must be a minimum in the volume expansivity of [emim][$CH_3CH_2SO_4$] at higher temperatures.[12] This same trend, which does not have a clear explanation, was described by Rodríguez et al. for ILs containing [$CH_3CH_2SO_4$], [CF_3SO_3], and [TFA] anions.[12] Our experimental volume expansivities for [emim][$CH_3CH_2SO_4$] [($5.48\cdot10^{-4}$ to $5.50\cdot10^{-4}$) K^{-1}] are very close to those obtained by Yang et al. ($5.37\cdot10^{-4}$ K^{-1}),[24] and by Rodríguez et al. [($5.43\cdot10^{-4}$ to $5.51\cdot10^{-4}$) K^{-1}].[12]

As in the case of the refractive index, to validate the experimental method comparison between our experimental densities of [emim][$CH_3CH_2SO_4$] and the literature data for the same IL was made. Thus, we have selected to compare the data from Jacquemin et al.,[8] Gómez et al.,[11] Rodríguez et al.,[12] Fernández et al.,[13] Matkowska et al.,[14] and Hofman et al.[15] because the principle of their measurements was the same as ours, the vibrating tube method. The percent deviations between experimental data and literature values were lower than 0.35 %,[8] 0.06 %,[11] 0.08 %,[12] 0.13 %,[13] 0.10 %,[14] and 0.28 %.[15] Taking into account the influence of the impurities in the IL on density, the experimental method seems sufficiently accurate.

The values for the densities of [emim][$CHF_2CF_2SO_3$] and [emim][$CH_3CH_2SO_4$] presented in this work have also been compared with the densities estimated by the group contribution method proposed by Ye and Shreeve,[25] and extended by Gardas and Coutinho.[26] In this estimation method, the only required parameter is the molecular volume of the IL calculated as the linear sum of the volumes of cation and anion. The density can be estimated as follows:

$$\rho = \frac{W}{NV_0(a + bT + cP)} \tag{8}$$

where ρ denotes the density in $kg\cdot m^{-3}$, W is the molecular weight of the IL in $kg\cdot mol^{-1}$, N is the Avogadro constant, V_0 is the molecular volume of the IL in $m^3\cdot molecule^{-1}$, T indicates the temperature in K, and P is the pressure in MPa. The constants a, b, and c obtained by Gardas and Coutinho were $8.005\cdot10^{-1}$ K, $6.652\cdot10^{-4}$ K, and $-5.919\cdot10^{-4}$ MPa, respectively. These fitting parameters were determined from 800 density data points for imidazolium-based ILs.[26]

The molecular volume of the [emim] cation was taken from literature (182 $Å^3$),[26] whereas the molecular volumes of [$CHF_2CF_2SO_3$] and [$CH_3CH_2SO_4$] anions were estimated as the difference between the molecular volume of [emim] cation and the molecular volumes of [emim][$CHF_2CF_2SO_3$] and [emim][$CH_3CH_2SO_4$] ILs, from experimental densities presented in this work. The values estimated for [$CHF_2CF_2SO_3$] and [$CH_3CH_2SO_4$] anions were 157 $Å^3$ and 135 $Å^3$, respectively. Thus, we are not using a pure contribution group method because the molecular volumes of the anion have been calculated from experimental data. However, these molecular volumes may be used to estimate the density of other 1,1,2,2-tetrafluoroethanesulfonate-based and ethylsulfate-based ILs.

Using the eq 8, the densities of [emim][$CHF_2CF_2SO_3$] and [emim][$CH_3CH_2SO_4$] were estimated at experimental temperature range. The calculated values are shown as dashed lines in Figure 2 along the experimental data. As can be seen, the estimated densities are very close to the experimental values at all temperatures, since the average percent deviations were 0.12 % for [emim][$CHF_2CF_2SO_3$] and 0.22 % for [emim][$CH_3CH_2SO_4$].

Viscosity. The dynamic viscosities of [emim][$CHF_2CF_2SO_3$] and [emim][$CH_3CH_2SO_4$] as a function of temperature are reported in Figure 4. As can be observed, the viscosities of both ILs are almost coincident at all of the temperature range. According to Bonhôte et al., the viscosity of ILs is governed by hydrogen bonding and van der Waals interactions.[27] The high viscosity of [emim][$CH_3CH_2SO_4$] is due to the formation of strong hydrogen bonding.[10]

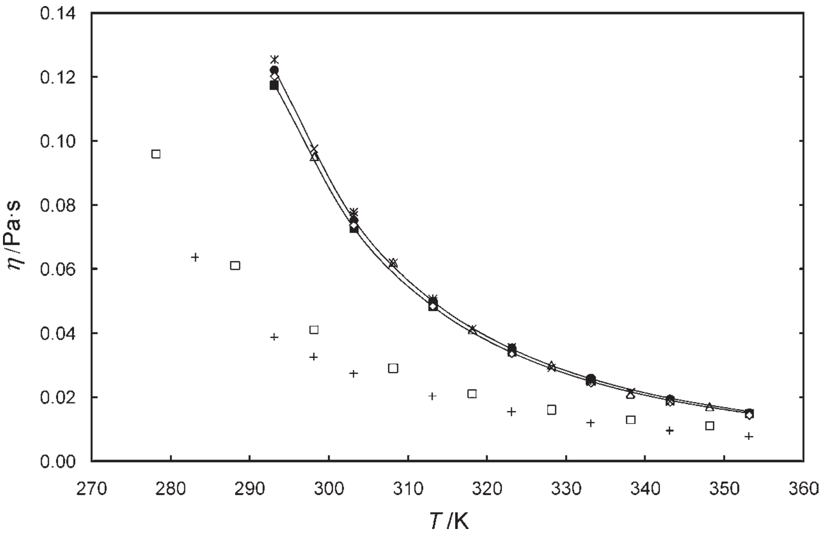

Figure 4. Dynamic viscosities as a function of temperature: ■, experimental values of [emim][$CHF_2CF_2SO_3$]; ●, Experimental values of [emim][$CH_3CH_2SO_4$]; Δ, [emim][$CH_3CH_2SO_4$] (from ref 12); ◊, [emim][$CH_3CH_2SO_4$] (from ref 13); *, [emim][$CH_3CH_2SO_4$] (from ref 10); ×, [emim][$CH_3CH_2SO_4$] (from ref 11); □, [emim][CF_3SO_3] (from ref 12); +, [emim][$(CF_3SO_2)_2N$] (from ref 21). Solid lines represent the fits obtained using VFT equation.

Literature data for the viscosities of [emim][CF_3SO_3][12] and [emim][$(CF_3SO_2)_2N$][21] are also shown in Figure 4. The viscosities of the two ILs are considerably lower than that of [emim][$CHF_2CF_2SO_3$]. This fact shows that the electrostatic interactions caused by the [$CHF_2CF_2SO_3$] anion are higher than those generated by the [CF_3SO_3] and [$(CF_3SO_2)_2N$] anions. The lower viscosity of the [emim][$(CF_3SO_2)_2N$] can be justified by the extensive charge delocalization in the bis(trifluoromethylsulfonyl)imide anion.[10] In short, the higher viscosity of the [emim]-[$CHF_2CF_2SO_3$] is due to a combination of strong interactions (hydrogen bonding and van der Waals forces) and a small charge delocalization in the 1,1,2,2-tetrafluoroethanesulfonate anion.

The most commonly used equation to relate viscosity to temperature in liquids is the Arrhenius law, defined as follows:

$$\eta = \eta_\infty \exp\left(-\frac{E_a}{RT}\right) \qquad (9)$$

where η_∞ is the viscosity at infinite temperature, E_a indicates the activation energy in $kJ \cdot mol^{-1}$, R is the ideal gas constant, and T is the measured temperature in K. For ILs, the Vogel–Fulcher–Tammann (VFT) equation[28–30] has been also widely used[11–13,31–33]

$$\eta = AT^{0.5} \exp\left(\frac{k}{T - T_0}\right) \qquad (10)$$

where A and k are adjustable parameters, T indicates the temperature in K, and T_0 is the ideal glass transition temperature in K. The fit parameters of eqs 9 and 10, and the correlation coefficients of the fits are given in Table 6. According to Seddon et al., the Arrhenius equation is suitable for ILs containing a cation with little symmetry.[34] Correlation coefficient values show that a better fit was achieved with the VFT equation than with the Arrhenius model. This fact is justified by the quite symmetrical structure of the imidazolium cation.

The validation of the results was performed by comparing the experimental measurements for [emim][$CH_3CH_2SO_4$] with data from the literature. The viscosity of this IL has been studied by several authors, and they employed different measurement methods. Fernández et al. utilized the same viscometer used in this work, an Anton Paar Automated Micro Viscometer (AMVn) based on the falling ball principle.[13] Gómez et al. used an automatic capillary viscometer Lauda PVS1,[11] Rodríguez et al. used a Brookfield DV-III cone and plate rheometer,[12] and Fröba et al. used a viscometer based on the surface light scattering method (SLS).[10] The results of the different works are plotted in Figure 4 along with the experimental data. The average absolute differences between our measurements and those from literature were 3.6 %,[13] 2.4 %,[11] 3.2 %,[12] and 2.3 %,[10] respectively. The deviations can be explained through the influence of impurities on the viscosity and the different measurement methods applied. Therefore, our viscosity data of [emim][$CHF_2CF_2SO_3$] and [emim][$CH_3CH_2SO_4$] ILs can be considered as reliable.

Table 6. Fitting Parameters of Arrhenius (eq 9) and Volger–Fulcher–Tammann (eq 10) Models Applied to the Viscosity of [emim][$CHF_2CF_2SO_3$] and [emim][$CH_3CH_2SO_4$] ILs

Arrhenius			VFT			
η_∞/ Pa·s	E_a/ $kJ \cdot mol^{-1}$	R^2	T_0/K	k/K	A/ Pa·s	R^2
			[emim][$CHF_2CF_2SO_3$]			
$2.31 \cdot 10^{-7}$	−31.99	0.997	170.30	808.34	$9.52 \cdot 10^{-6}$	0.999
			[emim][$CH_3CH_2SO_4$]			
$2.24 \cdot 10^{-7}$	−32.16	0.997	172.61	785.01	$1.06 \cdot 10^{-5}$	0.999

Surface Tension. Experimental surface tensions of [emim]-[$CHF_2CF_2SO_3$] and [emim][$CH_3CH_2SO_4$] at temperature range from 303.15 to 333.15 K are plotted in Figure 5. In order to analyze the influence of the anion on the surface tension, literature data for the surface tension of [emim][CF_3SO_3][35] and [emim][$(CF_3SO_2)_2N$][36,37] are also shown in the same figure.

Freire et al. and Torrecilla et al. studied the effect of anion structure on surface tensions of imidazolium-based ILs.[38,39] They

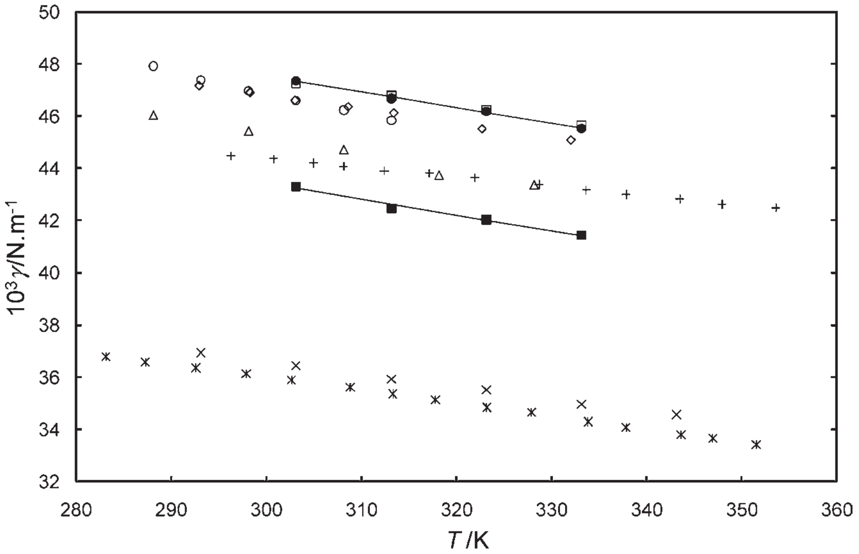

Figure 5. Surface tensions against temperature: ■, experimental values of [emim][$CHF_2CF_2SO_3$]; ●, experimental values of [emim][$CH_3CH_2SO_4$]; ◇, [emim][$CH_3CH_2SO_4$] (from ref 16); □, [emim][$CH_3CH_2SO_4$] (from ref 13); ○, [emim][$CH_3CH_2SO_4$] (from ref 11); Δ, [emim][$CH_3CH_2SO_4$] (from ref 17); +, [emim][CF_3SO_3] (from ref 35); ×, [emim][$(CF_3SO_2)_2N$] (from ref 36); *, [emim][$(CF_3SO_2)_2N$] (from ref 37). Solid lines represent the linear fits of the experimental data.

Table 7. Surface Enthalpy (H^γ), Surface Entropy (S^γ), Empirical Constant of Eötvös Equation (k), and Estimated Critical Temperature (T_c) of [emim][$CHF_2CF_2SO_3$] and [emim][$CH_3CH_2SO_4$] ILs

H^γ/ J·m^{-2}	S^γ/ J·m^{-2}·K^{-1}	k/ J·K^{-1}	T_c/K
	[emim][$CHF_2CF_2SO_3$]		
$6.15 \cdot 10^{-2}$	$6.03 \cdot 10^{-5}$	$1.52 \cdot 10^{-7}$	1289.2 ± 2.3
	[emim][$CH_3CH_2SO_4$]		
$6.53 \cdot 10^{-2}$	$5.93 \cdot 10^{-5}$	$1.41 \cdot 10^{-7}$	1417.4 ± 0.9

concluded that an increase in the size of the anion causes a decrease on the surface tension, and this trend is observed in Figure 5. The [emim][$(CF_3SO_2)_2N$] has the lower surface tension since the volume of the [$(CF_3SO_2)_2N$] anion is 248 Å^3.[26] The [emim][$CHF_2CF_2SO_3$] has an intermediate surface tension because the calculated volume of the [$CHF_2CF_2SO_3$] anion is 157 Å^3. Finally, the surface tensions of [emim][$CH_3CH_2SO_4$] and [emim][CF_3SO_3] are similar, as a result of the anion sizes. The estimated anion volume of the [$CH_3CH_2SO_4$] was 135 Å^3, and the size of the [CF_3SO_3] anion is 129 Å^3.[25]

The variation of surface tension of ILs with temperature can be considered linear.[39] The surface entropy, S^γ, and the surface enthalpy, H^γ, can be obtained from the linear fit of experimental data by using eqs 11 and 12.[38] The surface entropies and surface enthalpies of [emim][$CH_3CH_2SO_4$] and [emim][$CHF_2CF_2SO_3$] are listed in Table 7.

$$S^\gamma = -\frac{d\gamma}{dT} \tag{11}$$

$$H^\gamma = \gamma - T\left(\frac{d\gamma}{dT}\right) \tag{12}$$

The Eötvos equation has widely been used to relate surface tensions of ILs with temperature:[13,38,40,41]

$$\gamma \cdot \sqrt[3]{V_m^{\,2}} = k(T_c - T) \tag{13}$$

where γ is the surface tension in N·m^{-1}, V_m refers the molar volume in m^3·mol^{-1}, T_c is the critical temperature of the IL in K, T is the measured temperature in K, and k is a empirical constant calculated from the slope of the linear fit of $\gamma \cdot (V_m)^{2/3}$ against absolute temperature.[13] The empirical constant of Eötvos equation and estimated critical temperatures of [emim][$CH_3CH_2SO_4$] and [emim][$CHF_2CF_2SO_3$] ILs are also presented in Table 7. The values calculated for k are similar to the constant estimated by Restolho et al. These authors obtained k values between $(1.2 \cdot 10^{-7}$ and $2.7 \cdot 10^{-7})$ J·K^{-1}.[41] The estimated critical temperatures are in the range obtained by Freire et al. for several imidazolium-based ILs [(850 to 1600) K].[38] This method of estimating the critical temperature of an IL is widely used, although its reliability has been questioned recently.[42]

Volumetric properties of ILs can be estimated from surface tension data and they can be compared with those obtained from experimental densities. The interstice model proposed by Yang et al.[24] is based on four assumptions about packing of ions and the interstices between them in an IL. By using this model, the average volume of an interstice in an IL is given by

$$v = 0.6791\sqrt{\left(\frac{kT}{\gamma}\right)^3} \tag{14}$$

where k is the Boltzmann constant in J·K^{-1}, T indicates the experimental temperature in K, and γ is the surface tension in N·m^{-1}. The values obtained for the average volume of an interstice in the [emim][$CH_3CH_2SO_4$] and [emim][$CHF_2CF_2SO_3$] ILs at 303.15 K were $1.8 \cdot 10^{-29}$ m^3 and $2.0 \cdot 10^{-29}$ m^3, respectively. The interstice model proposes that the expansion of IL volume when temperature increases is only due to the expansion of the interstices. Hence, the volume expansivity can be estimated by using eq 15[24]

$$\alpha = \frac{1}{V_m}\left(\frac{\partial V_m}{\partial T}\right)_p = \frac{3N\nu}{V_m T} \qquad (15)$$

where N is the Avogadro constant. The estimated volume expansivity of [emim][$CH_3CH_2SO_4$] at 303.15 K was $5.56 \cdot 10^{-4}$ K^{-1}, whereas the value calculated for [emim][$CHF_2CF_2SO_3$] at the same temperature was $5.94 \cdot 10^{-4}$ K^{-1}. The differences between these values and the α calculated from density data are less than 1.2 %. Therefore, both estimation methods seem valid to accurately estimate the volume expansivity of an IL.

The validation of the results was performed by a comparison between experimental and literature surface tensions of [emim]-[$CH_3CH_2SO_4$]. As can be seen in Figure 5, literature data are quite different between them. This fact shows the important influence of impurities and the measurement method on surface tension measured. Among the impurities, water increases significantly the surface tension of this IL.[43] The mean percent deviations between the experimental and published surface tensions were 1.63 %,[11] 0.25 %,[13] 1.36 %,[16] and 5.17 %.[17] Our results for [emim][$CH_3CH_2SO_4$] seem sufficiently accurate to validate the experimental method.

CONCLUSIONS

Refractive indices, densities, and viscosities of the ILs [emim][$CH_3CH_2SO_4$] and [emim][$CHF_2CF_2SO_3$] were determined from (293.15 to 353.15) K at atmospheric pressure. Measurements of the surface tension of the two ILs were also performed at temperatures between (303.15 and 333.15) K. The reliabilities of the experimental methods were successfully tested by comparing the results obtained for [emim][$CH_3CH_2SO_4$] with literature data.

The experimental data of refractive index were fitted to a linear function of temperature. Temperature dependence of the density was correctly described by a quadratic polynomial equation, and the densities were estimated accurately using the group contribution method proposed by Ye and Shreeve and extended by Gardas and Coutinho. The viscosity data were fitted to Arrhenius and Vogel−Fulcher−Tamman (VFT) models, while the influence of temperature on surface tension was well described by the Eötvös equation.

The experimental values of the physical properties of [emim][$CHF_2CF_2SO_3$] and [emim][$CH_3CH_2SO_4$] were compared with published data of [emim][$(CF_3SO_2)_2N$] and [emim][CF_3SO_3] to describe the influence of the anion on the thermophysical properties studied. A higher molecular weight of the anion increases the density of an IL, whereas the surface tension decreases when the volume of the anion increases. The viscosity values of [emim][$CHF_2CF_2SO_3$] and [emim][$CH_3CH_2SO_4$] were quite similar at experimental temperature range. This fact highlights that the interactions caused by the 1,1,2,2-tetrafluoroethanesulfonate anion are of the same order of magnitude than those generated by the ethylsulfate anion.

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Funding Sources

The authors are grateful to the Ministerio de Ciencia e Innovación of Spain (MICINN) and the Comunidad de Madrid for financial support of Projects CTQ2008-01591 and S2009/PPQ-1545, respectively. S.G. also thanks MICINN for awarding her an FPI Grant (Reference BES-2009-014703) under the same project.

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