Effect of Cationic and Anionic Chain Lengths on Volumetric, Transport, and Surface Properties of 1-Alkyl-3-methylimidazolium Alkylsulfate Ionic Liquids at (298.15 and 313.15) K

José S. Torrecilla,*,† José Palomar,‡ Julián García,† and Francisco Rodríguez†

Departamento de Ingeniería Química, Universidad Complutense de Madrid, 28040 Madrid, Spain, and Sección de Ingeniería Química (Departamento de Química Física Aplicada), Universidad Autónoma de Madrid, Cantoblanco, 28049 Madrid, Spain

The effect of the alkyl chain of 1-alkyl-3-methylimidazolium alkylsulfate ([$C_n$mim][CH_3SO_4] and [$C_n$mim][$C_2H_5SO_4$] ionic liquids (ILs) with n between 1 to 8) on density, viscosity, and surface tension has been experimentally determined at (298.15 and 313.15) K. In addition, the quantum-chemical COSMO-RS method is used to extend the analysis of the influence of sulfate alkyl length on density by screening [$C_n$mim][$C_mH_{2m+1}SO_4$] compounds with m between 1 and 8. COSMO-RS is also tested for the first time in the prediction of IL viscosities. Density and surface tension of the ILs studied decrease with the number of carbon atoms in the alkyl substituent of cation, whereas viscosity increases. All of these properties decrease as the temperature increases.

Introduction

Ionic liquids (ILs) are chemicals composed of an organic cation and an inorganic or organic anion with a melting temperature below 373.15 K at atmospheric pressure and with negligible vapor pressure.[1,2] Because of the nature of the ions, the ILs exhibit mixed inorganic and organic characters.[2] Recently, because of their unique properties, ILs have attracted increasing attention as replacements for conventional organic solvents in catalysis, separation processes, electrochemistry, and many other fields.[2,3] In addition, one of the most attractive features of ILs is their ability to be tailormade for a specific purpose by careful selection of the cation, anion, or both.[3,4] However, given that there are $\sim 10^6$ ILs,[3] the selection or design of the most suitable IL for a given application would be greatly assisted by theoretical models.[5,6]

Currently, a large quantity of ILs is available commercially or by synthesis.[3] The most commonly studied are ILs based on imidazolium cations. In the petrochemical field, ILs based on alkylsulfate anions are one of the types of ILs with a wider application in the extraction processes; for example, the extraction of sulfur and nitrogen compounds from gasoline and diesel by 1-butyl-3-methylimidazolium octylsulfate and 1-ethyl-3-methylimidazolium ethylsulfate is being used as an alternative to common hydrodesulfurization.[7,8] Meindersma et al. stated that 1-ethyl-3-methylimidazolium ethylsulfate, 1,3-dimethylimidazolium methylsulfate, and 1-butyl-3-methylimidazolium methylsulfate are suitable for extraction of toluene from toluene and heptane mixtures.[9,10] Arce et al. carried out the separation of *tert*-amyl ethyl ether and ethanol from their mixtures by alkyl sulfate ILs.[11] Deenadayalu et al. stated that 1-ethyl-3-methylimidazolium octylsulfate and 1-methyl-3-octylimidazolium diethylenglycol monomethyl ether sulfate are potential solvents for the separation of aromatic compounds from alkanes.[12,13]

* Corresponding author. Tel: +34 91 394 42 40. Fax: +34 91 394 42 43. E-mail: jstorre@quim.ucm.es.
† Universidad Complutense de Madrid.
‡ Universidad Autónoma de Madrid.

Because of this important application of the ILs based on alkyl sulfates, a considerable amount of data related to this type of IL are being reported, [14−17] but, to the best of our knowledge, a detailed study related to the influence of temperature and alkyl length of the cation and anions on the volumetric, transport, and surface properties has not been reported. Therefore, the main objective of this work was the determination of density, viscosity, and surface tension for the IL family of 1-alkyl-3-methylimidazolium alkylsulfate at (298.15 and 313.15) K. For this purpose, the properties of two commercially available ILs [1,3-dimethylimidazolium methylsulfate ([C_1mim][CH_3SO_4]) and 1-ethyl-3-methylimidazolium ethylsulfate ([C_2mim][$C_2H_5SO_4$])] and six ILs synthesized by Green Solutions Chemicals S. L. (Plaza Fernando Conde Montero, 9, 36201 Vigo (Pontevedra), Spain) for this work, [1-butyl-3-methylimidazolium methylsulfate ([C_4mim][CH_3SO_4]), 1-hexyl-3-methylimidazolium methylsulfate ([C_6mim][CH_3SO_4]), 1-octyl-3-methylimidazolium methylsulfate ([C_8mim] [CH_3SO_4]), 1-butyl-3-methylimidazolium ethylsulfate ([C_4mim][$C_2H_5SO_4$]), 1-hexyl-3-methylimidazolium ethylsulfate ([C_6mim][$C_2H_5SO_4$]), and 1-octyl-3-methylimidazolium ethylsulfate ([C_8mim][$C_2H_5SO_4$]), were measured. In addition, the a priori COSMO-RS method was tested to estimate densities and viscosities of this family of 1-alkyl-3-methylimidazolium alkylsulfates at 298.15 K[18] using a simple molecular model of ion pairs to simulate the IL fluid.

Experimental Section

Chemicals. From Green Solutions Chemicals S. L., we obtained [C_1mim][CH_3SO_4] (≥ 98 % purity); [C_6mim][CH_3SO_4] (≥ 98 % purity); [C_8mim][CH_3SO_4] (≥ 98 % purity); [C_4mim][$C_2H_5SO_4$] (≥ 98 % purity); [C_6mim][$C_2H_5SO_4$] (≥ 98 % purity); and [C_8mim][$C_2H_5SO_4$] (≥ 98 % purity). From Sigma-Aldrich Chemie GmbH, we obtained [C_4mim][CH_3SO_4]) (≥ 95 % purity) and [C_2mim][$C_2H_5SO_4$] (≥ 95 % purity). The water mass fraction, determined by Karl Fischer method (Karl Fischer titrator DL31 from Mettler Toledo), was less than $2 \cdot 10^{-3}$ for all of the ILs studied. All samples were dried by heating to

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Table 1. Experimental and COSMO-RS Density, ρ, Values of $[C_n mim][CH_3SO_4]$ and $[C_n mim][C_2H_5SO_4]$ (n between 1 and 8 Carbon Atoms)

	ρ/g·cm^{-3}					
	T/K = 298.15				T/K = 313.15	
	$[C_n mim][CH_3SO_4]$		$[C_n mim][C_2H_5SO_4]$		$[C_n mim][CH_3SO_4]$	$[C_n mim][C_2H_5SO_4]$
n	exptl	COSMO	exptl	COSMO	exptl	exptl
1	1.32838	1.376		1.331	1.31785	
2		1.323	1.23626	1.283		1.22679
3		1.287		1.248		
4	1.21295	1.243	1.19893	1.220	1.19975	1.18869
5		1.219		1.193		
6	1.16883	1.192	1.15060	1.173	1.15887	1.14060
7		1.171		1.153		
8	1.11447	1.161	1.11593	1.139	1.10464	1.10620

333.15 K for 24 h under reduced pressure. Then, in all experiments, every pretreatment (filling and sealing of capillary) was carried out in a controlled atmosphere glovebox under dry nitrogen because of the highly hygroscopic nature of these ILs. Because of this, the ILs' moisture was assumed to be constant throughout the measurement. The means of three replicate measurements were reported.

Density Measurements. The densities of $[C_1mim][CH_3SO_4]$, $[C_4mim][CH_3SO_4]$, $[C_6mim][CH_3SO_4]$, $[C_8mim][CH_3SO_4]$, $[C_2mim][C_2H_5SO_4]$, $[C_4mim][C_2H_5SO_4]$, $[C_6mim][C_2H_5SO_4]$, and $[C_8mim][C_2H_5SO_4]$ were determined at (298.15 and 313.15) K ($\pm$ 0.01 K) at atmospheric pressure using an Anton Paar DMA 5000 oscillating U-tube densimeter (Anton Paar GmbH, Graz, Austria). These measurements have been carried out taking into account the viscosity of the sample (viscosity correction). The uncertainty in the experimental measurements was found to be less than $\pm$ 1·10^{-5} g·cm^{-3}. To validate the equipment and the method used, the density of ultrapure water was determined, and the measurements are in agreement with literature values.[19]

Dynamic Viscosities. Dynamic viscosities of $[C_1mim][CH_3SO_4]$, $[C_4mim][CH_3SO_4]$, $[C_6mim][CH_3SO_4]$, $[C_8mim][CH_3SO_4]$, $[C_2mim][C_2H_5SO_4]$, $[C_4mim][C_2H_5SO_4]$, $[C_6mim][C_2H_5SO_4]$, and $[C_8mim][C_2H_5SO_4]$ were determined at two temperatures, (298.15 and 313.15) K, using an Anton Paar AMVn automated rolling ball microviscometer (Anton Paar GmbH, Graz, Austria).[20] Because the principle of measurement is based on a falling ball in a capillary, proper validation of the capillaries was achieved, as was described in the literature at working temperatures.[17] The uncertainty in the experimental measurements has been found to be less than $\pm$ 0.01 mPa·s.

Surface Tension. Surface tension measurements of $[C_1mim][CH_3SO_4]$, $[C_4mim][CH_3SO_4]$, $[C_6mim][CH_3SO_4]$, $[C_8mim][CH_3SO_4]$, $[C_2mim][C_2H_5SO_4]$, $[C_4mim][C_2H_5SO_4]$, $[C_6mim][C_2H_5SO_4]$, and $[C_8mim][C_2H_5SO_4]$ were performed using a Dataphysics OCA 15 plus pendant drop tensiometer (Dataphysics Instruments GmbH, Filderstadt), which is based on the pendant drop method.[21] An electronic syringe unit was used to form IL drops at the lower end of the dosing needle inside a thermal chamber thermostatted using a JULABO F12-EC bath with a temperature stability of $\pm$ 0.03 K at two temperatures, (298.15 and 313.15) K. The drop shape is snapped from the images taken from a charge-coupled device camera to infer the surface tension using suitable software (SCA 20 from Dataphysics Instruments GmbH). The validation of equipment is described in the literature.[17] The uncertainty of the surface tension measurements was estimated to be less than $\pm$ 0.05 mN·m^{-1}.

Computational Details. The molecular geometry of all compounds (common solvents and ILs) was optimized at the B3LYP/6-31++G** computational level in the ideal gas phase using a quantum chemical Gaussian03 package.[22] Using a molecular model to simulate the pure IL, ion-paired structures including both counterions were optimized as a whole. Then, the standard procedure was applied to COSMO-RS calculations, which consist of two steps: First, Gaussian 03 was used to compute the COSMO files. The ideal screening charges on the molecular surface for each species were calculated by the continuum solvation COSMO model using the BVP86/TZVP/DGA1 level of theory. Subsequently, COSMO files were used as input in COSMOtherm statistical thermodynamic code to calculate the specific density and viscosity of the chemical species studied at 298 K.[23] According to our chosen quantum method, the functional and basis sets, the corresponding parametrization (BP_TZVP_ C21_0105) that is required for the calculation of physicochemical data and that contains intrinsic parameters of COSMOtherm, and element specific parameters were used.

Results and Discussion

The density data obtained in this work for pure $[C_4mim][CH_3SO_4]$ and $[C_2mim][C_2H_5SO_4]$ are in agreement with density values, ρ, reported in literature. (The differences between experimental data and those reported in literature are 0.18 %,[14] 0.40 %,[24] 0.15 %,[25] 0.06 %,[26] 0.57 %,[27] and 0.07 %.[28]) Given the important influence of the impurities content of the abovementioned commercial ILs on their viscosity values, the difference between the experimental data (vide supra) and those values of viscosity reported in the literature (where the ILs used were synthesized by each research group) is less than 5 %.[14,25] The values obtained for the surface tension of $[C_4mim][CH_3SO_4]$, $[C_1mim][CH_3SO_4]$, and $[C_2mim][C_2H_5SO_4]$ are in agreement with the data reported in literature (< 0.4 %,[14] < 0.6 %, and < 1.7 %,[26,29] respectively).

Density of 1-Alkyl-3-methylimidazolium Alkylsulfate Ionic Liquids. The measured density values of $[C_n mim][CH_3SO_4]$ and $[C_n mim][C_2H_5SO_4]$ ILs with n between 1 and 8 are shown in Table 1. As can be observed, the density decreases as the alkyl chain length and temperature increase. To complete the current results, COSMO-RS calculations of density at 298.15 K have been carried out for $[C_n mim][C_m H_{2m+1}SO_4]$ compounds with n and m between 1 and 8. As can be seen in Figure 1, the correspondence between experimental and COSMO-RS (Supporting Information) predictions is equally good for 1-alkyl-3-methylimidazolium alkylsulfates and other imidazolium-based ILs and common organic solvents (alcohols). The root-mean-square deviation (rmsd) is less than 2.7 %.[5] Experimental and calculated values (Figure 2) evidence a reduction in density with the length of the alkyl group in both cation and anion, and these trends are in agreement with the literature.[30,31] In accordance with the equations shown in Table 2, which were obtained from

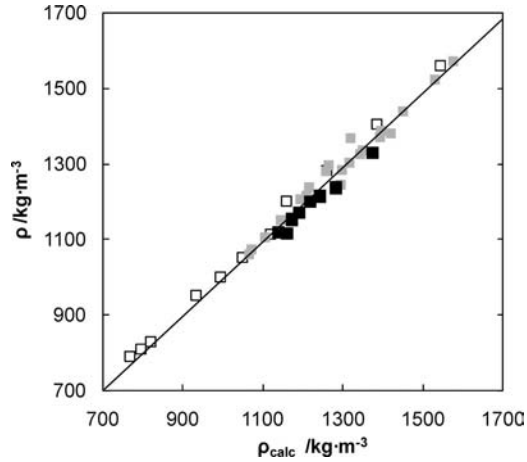

Figure 1. Comparison of experimental ρ and COSMO-RS ρ_{calc} values of density for: ■, 1-alkyl-3-methylimidazolium alkylsulfates; shaded squares, other imidazolium-based ILs; □, common solvents (alcohols) at 298 K.[37,39] (The ILs and common solvents and their density estimations are shown in the Supporting Information).

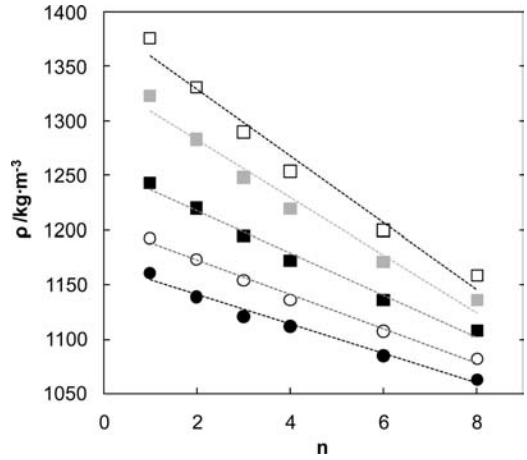

Figure 2. COSMO-RS analysis of the influence of the alkyl chain (n) on density for 1-alkyl-3-methylimidazolium alkylsulfates [$C_n$mim][$C_mH_{2m+1}SO_4$] at 298 K (□, $n = 1$; shaded squares, $n = 2$; ■, $n = 4$; ○, $n = 6$; ●, $n = 8$). (The ILs and their density estimations are shown in the Supporting Information).

Table 2. Adjusted Regression Coefficient and Statistic of the Fits Obtained from the Regression Models of COSMO-RS Density, ρ, Values of Ionic Liquids (n between 1 and 8) at 298.15 K[a]

ionic liquids	α_0[b]	α_1[b]	R_a^2	σ/g·cm^{-3}
[$C_n$mim][CH_3SO_4]	1.40	−0.036	0.98	$1\cdot10^{-2}$
[$C_n$mim][$C_2H_5SO_4$]	1.35	−0.031	0.97	$1\cdot10^{-2}$
[$C_n$mim][$C_3H_7SO_4$]	1.27	−0.023	0.98	$6\cdot10^{-3}$
[$C_n$mim][$C_4H_9SO_4$]	1.21	−0.018	0.98	$5\cdot10^{-3}$
[$C_n$mim][$C_6H_{13}SO_4$]	1.17	−0.015	0.99	$4\cdot10^{-3}$
[$C_n$mim][$C_8H_{17}SO_4$]	1.16	−0.013	0.98	$4\cdot10^{-3}$

[a] ILs used and their density estimations are shown in the SI. [b] ρ/g·cm$^{-3} = \alpha_0 + \alpha_1 n$.

COSMO-RS predictions, the density values linearly depend on the alkyl chain length of the cation, with adjusted correlation coefficients (R_a^2) greater than 0.97 and standard deviations (σ) less than $1\cdot10^{-2}$ g·cm^{-3}, in agreement with previous evidence.[32] Gardas et al. have also reported linear relations between the number of carbons of cation and the density values ($R^2 > 0.99$) for the family of imidazolium ILs based on bis-(trifluoromethylsulfonyl)imide anion.[33] Similar linear density dependence on the length of the alkyl chain of the sulfate anion is obtained in the work of Gardas et al. (Figure 2). Compounds with larger octyl groups slightly deviate from the linear trend for all cases studied. This behavior was also observed for other series of imidazolium-based ILs.[5]

Table 3. Viscosity, η, Values of [$C_n$mim][CH_3SO_4] and [$C_n$mim][$C_2H_5SO_4$] (n between 1 and 8 Carbon Atoms)

	η/mPa·s			
	T/K = 298.15		T/K = 313.15	
n	[$C_n$mim][CH_3SO_4]	[$C_n$mim][$C_2H_5SO_4$]	[$C_n$mim][CH_3SO_4]	[$C_n$mim][$C_2H_5SO_4$]
1	75.5		40.8	
2		91.8		48.5
4	213[a]	379.1	104.2	164.0
6	383.0	589.0	164.3	236.0
8			180.6	275.2

[a] Ref 14.

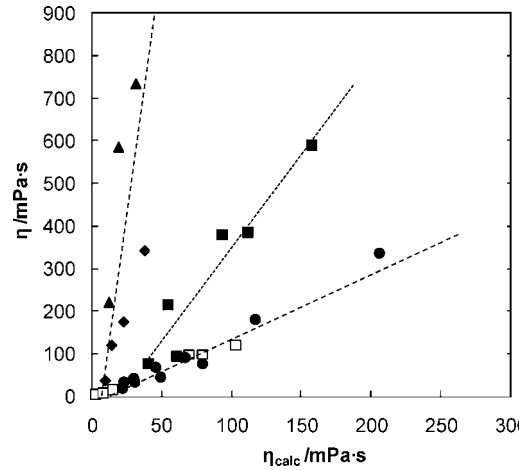

Figure 3. Comparison of experimental and COSMO-RS calculated values of viscosity for: ■, 1-alkyl-3-methylimidazolium alkylsulfates; other imidazolium-based ILs (◆, IL-BF_4; ▲, IL-PF_6; ●, other ILs); □, common solvents (alcohols) at 298 K.[37,39,40] (The ILs and common solvents and their viscosity estimations are shown in the Supporting Information).

Viscosity of 1-Alkyl-3-methylimidazolium Alkylsulfate Ionic Liquids. The viscosity values, η, of [$C_n$mim][CH_3SO_4]and [$C_n$mim][$C_2H_5SO_4$] ILs with n between 1 and 8 are shown in Table 3. As can be observed, the viscosity decreases as temperature increases and rises with the alkyl chain length of the cation. This trend is in agreement with the literature.[34] However, as can be seen in Table 3, ILs based on higher anion sizes also present higher viscosity values. This point is in agreement with the literature.[14,35,36] In addition, the COSMO-RS method is tested here for the first time to estimate viscosity values for ILs. The calculations of alcohol viscosities are also included in the analysis as references of common solvents. As can be seen in Figure 3, COSMO-RS does not provide accurate predictions of IL viscosity; this property is underestimated in the function of the type of anion. The viscosity dependence on the alkyl chain length (Figure 4a) shows a trend for [$C_n$mim][CH_3SO_4] and [$C_n$mim][$C_2H_5SO_4$] families of ILs that is similar to those found in the 1,2- and 1,n-alkanediols, respectively (Figure 4b).[37] However, COSMO-RS predicts a qualitatively incorrect exponential increase in viscosity values with the number of carbon atoms of the cation alkyl substituent for the [$C_n$mim][$C_2H_5SO_4$] family (Figure 4a), even when this tendency is well predicted for the case of 1,n-alkanediols (Figure 4b).

Surface Tension of [$C_n$mim][CH_3SO_4] and [$C_n$mim][$C_2H_5SO_4$] Ionic Liquids. The surface tension, γ, of [$C_n$mim][CH_3SO_4] and [$C_n$mim][$C_2H_5SO_4$] with n between 1 and 8 is shown in Table

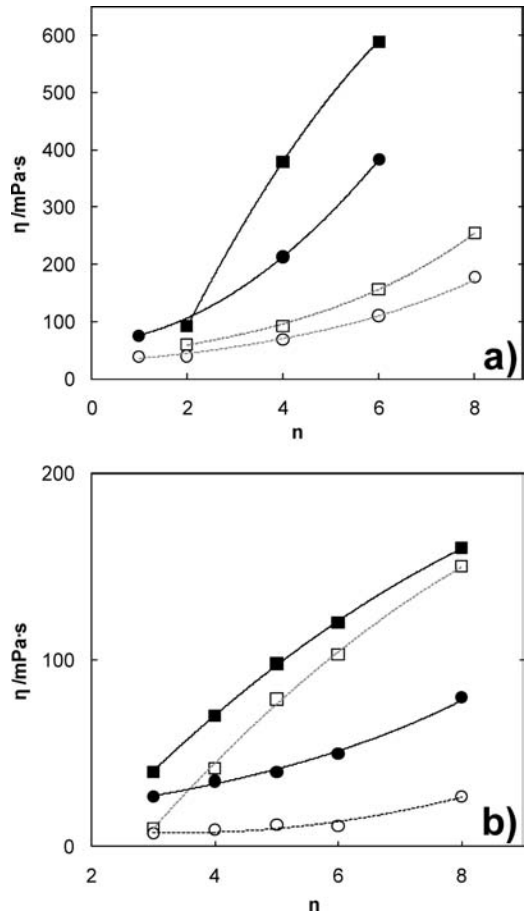

Figure 4. Experimental and COSMO-RS viscosity values against the number of carbon atoms of the alkyl chain (n) on viscosity for (a) $[C_n\text{mim}][CH_3SO_4]$ (○, calculated at 298.15 K; ●, experimental at 298.15 K) and $[C_n\text{mim}][C_2H_5SO_4]$ (□, calculated at 298.15 K; ■, experimental at 298.15 K) ionic liquids and (b) 1,2- (○, calculated; ● experimental) and 1,n-alkanediols (□, calculated; ■, experimental) at 298.15 K.[37]

Table 4. Surface Tension, γ, Values of $[C_n\text{mim}][CH_3SO_4]$ and $[C_n\text{mim}][C_2H_5SO_4]$ (n between 1 and 8 Carbon Atoms)

	γ/mN·m			
	T/K = 298.15		T/K = 313.15	
n	$[C_n\text{mim}][CH_3SO_4]$	$[C_n\text{mim}][C_2H_5SO_4]$	$[C_n\text{mim}][CH_3SO_4]$	$[C_n\text{mim}][C_2H_5SO_4]$
1	59.42		58.99	
2		45.43[a]		46.78
4	43.3	36.38	42.09	33.91
6	33.59	31.77	33.54	29.63
8	30.41	28.67	30.03	27.94

[a] Ref 38.

4. The surface tension decreases as temperature increases, and it increases as imidazolium cation size decreases. This trend and the surface tension values agree with the literature. In particular, in two works reported by Pereiro et al., the surface tensions of 1,3-dimethylimidazolium methylsulfate and 1-butyl-3-methylimidazolium methylsulfate are determined.[14,29] However, the surface tension of $[C_2\text{mim}][C_2H_5SO_4]$ does not follow this trend (increases less than 3 % with the temperature, Table 4). Because this surface tension was taken from literature, the comparison is not reliable. The surface tension values determined by Wandschneider et al. also decrease with temperature.[38] As can be seen in Figure 5, the surface tension increases as the number of carbon atoms of the alkyl chain of cation decreases. In light of these results, the surface tension starts to show saturation around 30 mN·m.

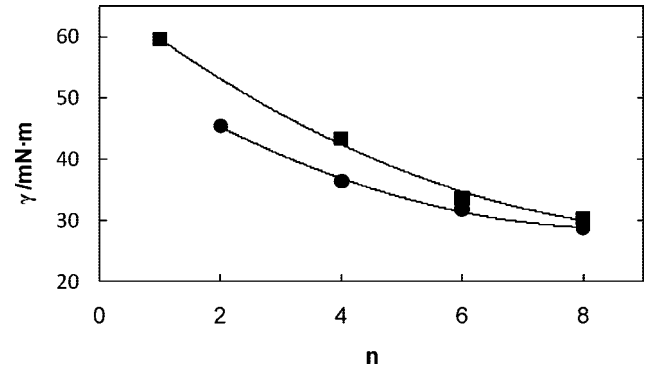

Figure 5. Experimental surface tension values against the number of carbon atoms of the alkyl chain (n) at 298.15 K (■, $[C_n\text{mim}][CH_3SO_4]$; ●, $[C_n\text{mim}][C_2H_5SO_4]$).

Conclusions

In this work, the effect of alkyl chain length and temperature on density, viscosity, and surface tension for the family of $[C_n\text{mim}][C_mH_{2m+1}SO_4]$ ILs (with n and m between 1 and 8) has been studied. In the case of density, a linear decrease is found for the values of this property with the number of carbon atoms of the alkyl chain of both cation and anion. Surface tension is also found to decrease as the cation alkyl chain increases. However, the viscosity of the sulfate ILs increases significantly with the size of the imidazolium substituent, with a similar trend to that found for 1,n-alkanediols. As expected, the density, viscosity, and surface tension of the studied ILs decrease as the temperature increases. Given its satisfactory performance, the COSMO-RS method to predict densities of ILs was applied to complete the analysis of the alkyl chain influence. In contrast, viscosity values were found to not be accurately predicted by COSMO-RS using a simple molecular model of ion-pair structures.

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Supporting Information Available:

Experimental values of density and viscosity and COSMO-RS estimations of ILs and alcohols used. This material is available free of charge via the Internet at http://pubs.acs.org.

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