1-Alkyl-3-methylimidazolium alkanesulfonate ionic liquids, $[C_nH_{2n+1}mim][C_kH_{2k+1}SO_3]$: synthesis and physicochemical properties†

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A set of 1-alkyl-3-methylimidazolium alkanesulfonate ionic liquids, $[C_nmim][C_kSO_3]$, formed by the variation of the alkyl chain lengths both in the cation and the anion (n = 1–6, 8, or 10; k = 1–4, or 6), was synthesised, with sixteen of them being novel. The ionic liquids were characterised by ^1H and ^{13}C NMR spectroscopy, and mass spectrometry. Their viscosities and densities as a function of temperature, as well as melting points and decomposition temperatures, were determined. The molecular volumes, both experimental and calculated, were found to depend linearly on the sum (n + k).

Introduction

Ionic liquids have recently received much attention as possible alternatives to volatile organic compounds.[1] They can replace more conventional media to perform chemical reactions, to support homogeneous or heterogeneous catalytic processes, or to carry out extractions and separations. A broad range of possible cations and anions allows us to create diverse ionic liquids, tailored to various needs,[2] but there have been few studies in which both the cation and the anion have been systematically varied.[3,4] In this work, a family of ionic liquids based on alkanesulfonate anions, $[C_kSO_3]^-$, and 1-alkyl-3-methylimidazolium cations, $[C_nmim]^+$, where lengths of the linear alkyl side chains were varied independently, was prepared (Fig. 1). A two-stage synthetic route to prepare these compounds has recently been reported;[5] however, these syntheses were not strategically performed in a systematic manner to obtain a matrix-like family of ionic liquids, nor was a detailed and more complete physicochemical characterisation of the resulting salts attempted.

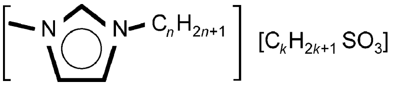

Fig. 1 Structure of $[C_nmim][C_kSO_3]$ ionic liquids.

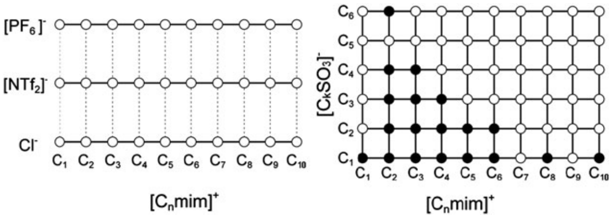

Fig. 2 Schematic representations showing different families of ionic liquids; in (left), members of the 1-alkyl-3-methylimidazolium family are shown with different anions, defining traditional homologous series (different series represented by the solid lines) that can be correlated whenever two ionic liquids have a common cation (dashed lines); in (right), members of the $[C_nmim][C_kSO_3]$ ionic liquid family are shown. This family is characterised by a matrix-like arrangement of its members (solid lines). The filled dots represent ionic liquids synthesised and characterised in the present study.

Traditionally, an ionic liquid family is established by using one fixed anion or cation and varying the nature of the counter-ion in a systematic way—*i.e.* by increasing the alkyl side chain length in a homologous series, or varying the degree of substitution. Here, the family of ionic liquids was designed by altering the nature of both the cation and the anion in a systematic way, and thus creating a two-dimensional matrix of ionic liquids (see Fig. 2). This work aims to discover if there are any correlations between the structure and properties within this new family of ionic liquids. This is important *per se* especially if one considers that the length of an alkyl side chain appended to a *cationic* polar head can determine the existence and the morphology of apolar nano-domains in neat ionic liquids. New fundamental structural issues will naturally emerge if one considers the present case in which alkyl side chains of different lengths can be attached to the cation, to the anion, or to both.

It is also interesting to investigate how these ionic liquids (based on alkanesulfonates) differ, in terms of their physicochemical properties, from the related alkanesulfate family, $[C_kSO_4]^-$, especially as the latter has been suggested as a set of particularly environmentally friendly ionic liquids[6,7] and,

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more recently, as potential candidates to be used in the construction of a liquid-mirror lunar telescope.[8]

A series of 1-alkyl-3-methylimidazolium alkanesulfonate ionic liquids, $[C_n\text{mim}][C_kSO_3]$ (n = 1–6, 8, or 10; k = 1–4, or 6) was prepared (see Fig. 2), and their melting points, decomposition temperatures, and density and viscosity as a function of temperature were determined.

Experimental

Instrumental procedures

NMR spectroscopy. All NMR spectra were recorded on a Bruker Avance spectrometer DPX 300 at 27 °C, using deuterated trichloromethane as solvent (10–20 mM solutions for ^{1}H NMR spectroscopy).

Mass spectrometry. All mass spectra of ionic liquids (diluted solution in ethanenitrile) were recorded using a Waters LCT PREMIER Electrospray mass spectrometer.

Karl Fischer analysis. The water content of ionic liquids was measured by coulometric Karl Fischer (Metrohm) titration. Ionic liquids were tested immediately after drying under high vacuum, and the water content was below 150 ppm for all samples.

Differential scanning calorimetry (DSC). The melting points of the synthesised ionic liquids were measured by DSC, using a TA Instruments Modulated DSC 2920. Cooling was accomplished by using a refrigerated cooling system capable of controlling the temperature down to 220 K. Dry nitrogen gas (flow rate of *ca.* 20 cm^3 min^{-1}) was purged through the DSC cell. The heating/cooling regime was adjusted for each sample separately.

Typically, for solid 1-alkyl-3-methylimidazolium alkanesulfonates, a standard heating and cooling ramp of 5 K min^{-1} was used. For liquid samples, including supercooled ionic liquids, much lower cooling and heating rates were used (0.2 to 1 K min^{-1}). Both the onset and the peak melting temperatures were measured and, for each ionic liquid, the enthalpy of fusion was determined by integration of the experimental heat flow curves as functions of temperature. In some cases it was impossible to detect the phase transitions (crystallisation and melting) using the DSC cell. Therefore, for $[C_2\text{mim}][C_2SO_3]$, $[C_2\text{mim}][C_3SO_3]$, $[C_2\text{mim}][C_4SO_3]$, and $[C_6\text{mim}][C_1SO_3]$, seeds were used to trigger crystallisation in supercooled ionic liquid samples. This procedure could not be implemented in the DSC cell due to the small size of the samples used in that case. As a consequence, the samples were heated slowly in a small glass vial, and melting points were determined visually as the temperature of the disappearance of the last crystal. In this case, the uncertainty of the melting point temperatures (±3 K in most cases) is much greater than that of measurements in the DSC cell (or even that of commercial capillary melting point instruments). The use of small vials instead of capillary tubes in this case is related to the handling of the viscous ionic liquid samples.

Thermogravimetric analysis (TGA). Decomposition temperature measurements were performed in a TA Instruments Q50 thermogravimetric analyser. The measurements were done in platinum pans, at a heating rate of 10 K min^{-1}, in air. The onset of the weight loss in each thermogram was used as a measure of the decomposition temperature.

Density measurements. Density was measured with an Anton Paar vibrating tube densimeter, model DMA 5000, operating at atmospheric pressure and within the temperature range 293 to 333 K.

The internal calibration of the instrument was confirmed by measuring the densities of atmospheric air and doubly distilled water, according to the recommendations of the manufacturer. The DMA 5000 cell was embedded in a metallic block, the temperature of which was controlled by several Peltier units. This arrangement allowed a temperature stability better than ±2 mK.

All ionic liquids used in the density determinations were degassed under vacuum and moderate temperature conditions for periods longer than 24 h and stored in sealed vials prior to injection in the densimeter, using non-lubricated disposable syringes.

Viscosity measurements. The viscosity was determined using a rheometer, Rheometrics Scientific SR200, that allows measurements from 293 to 393 K at atmospheric pressure, and in a wide viscosity range (1 to 3000 mPa s) depending on the geometry used. A Couette geometry (concentric cylinders) was chosen for this study. Temperature was maintained constant to within 0.01 K by means of a recirculating bath and was measured with the same accuracy using a platinum resistance thermometer (PRT) from Hart Scientific (model 5612, accuracy of ±0.018 °C at 0 °C), calibrated against a secondary reference temperature standard. To decrease the water contamination of the sample during the measurements, the rheometer was placed inside a glove-box in an isolating atmosphere of purified and dried air.

In order to improve the accuracy of the viscosity measurements, the rheometer was calibrated, as a function of temperature, with the standard viscosity oil N100 from Cannon Instrument Company (280 mPa s at 293 K).

Viscosity measurements were performed in steps of approximately 10 K from 293 K up to 360 K in all the ionic liquid samples in which a sufficient amount (*ca.* 14 cm^3) was available. Similar measurements performed before in the same equipment[9] permitted a statistical analysis of the results that has indicated a precision in the viscosities of 0.2% and an overall uncertainty lower than 1%. The same precision cannot be claimed in the present measurements due to the problems related to the hygroscopic behaviour of ionic liquids (see two paragraphs above). An overall uncertainty of around 10% was estimated in this case, inferred from experiments where the determinations were cycled over time and temperature in order to check the reproducibility of the viscosity data.

Materials

The nineteen ionic liquids used in this study were synthesised following the procedure described below. These include $[C_n\text{mim}][C_1SO_3]$, n = 1–6, 8 or 10; $[C_n\text{mim}][C_2SO_3]$,

n = 2–6; [C$_n$mim][C$_3$SO$_3$], n = 2, 3, or 4; [C$_n$mim][C$_4$SO$_3$], n = 2 or 3; and [C$_2$mim][C$_6$SO$_3$] (Fig. 2).

1-Methylimidazole (≥ 99%; Aldrich) was purified by distillation from sodium hydroxide immediately prior to use. Dichloromethane, ethyl ethanoate, ethyl methanesulfonate (≥ 98%), ethanesulfonyl chloride (≥ 99%), 1-propanesulfonyl chloride (≥ 98%), 1-butanesulfonyl chloride (≥ 98%), 1-propanol (≥ 99.8%), 1-butanol (≥ 99.8%), 1-hexanol (≥ 99.5%), 1-octanol (≥ 99%), 1-decanol (≥ 99%), sodium hexanesulfonate (98%), and trimethylamine (≥ 99%) were purchased from Aldrich and used as received. Methyl methanesulfonate, $CH_3SO_3CH_3$ (99%), was purchased from Acros Organics.

Synthetic procedures

All but three ionic liquids, 1,3-dimethylimidazolium methanesulfonate, 1-ethyl-3-methylimidazolium hexanesulfonate, and 1-ethyl-3-methylimidazolium methanesulfonate, were prepared in two stages, as discussed in ref. 5 and also below in more detail. All procedures were performed under dry nitrogen.

(i) Syntheses of alkanesulfonate esters. Alkan-1-ol ($C_nH_{2n+1}OH$; n = 2–10) (1.1 mol eq.) and triethylamine (1.1 mol eq.) were dissolved in dichloromethane (430 cm^3), placed in a round-bottomed flask (fitted with a thermometer), and stirred vigorously. The mixture was cooled in an ice-bath, and alkylsulfonyl chloride ($C_kH_{2k+1}SO_2Cl$, k = 1–4, or 6) (1 mol eq.) dissolved in dichloromethane (100 cm^3) was added dropwise to maintain a reaction temperature below 0 °C. The reaction mixture was then stirred for several hours at room temperature (monitored by ^{1}H NMR spectroscopy), until a white solid precipitated. The solid was removed by filtration, and dichloromethane was removed using a rotary evaporator to yield the crude liquid product. This was purified by fractional vacuum distillation to yield a colourless liquid. Details of individual syntheses are given in Table 1.

(ii) Syntheses of 1-alkyl-3-methylimidazolium alkanesulfonate ionic liquids. The freshly distilled alkyl alkanesulfonate ester ($C_nH_{2n+1}SO_3C_kH_{2k+1}$) (1.1 mol eq.) and 1-methylimidazole (1 mol eq.) were placed in a round-bottomed flask and dissolved in ethyl ethanoate (150 cm^3). The reaction mixture was stirred under reflux for several hours. Upon completion of the reaction, the crude product (lower ionic liquid layer) was washed six times with ethyl ethanoate (*ca.* 50 cm^3) and the remaining solvent removed under reduced pressure to yield the pure product. Details of individual syntheses are given in Table 2.

Table 1 Masses of reactants (m) and reaction conditions (reaction time, t) for the synthesis of alkanesulfonate esters, $C_kH_{2k+1}SO_3C_nH_{2n+1}$

		m/g			
k	n	$C_nH_{2n+1}OH$	NEt_3	$C_kH_{2k+1}SO_2Cl$	t/h
1	3	21.5	46.1	37.3	12
	4	32.0	49.9	45.2	12
	5	29.2	42.6	43.5	12
	6	37.4	42.1	38.1	48
	8	—	—	—	48
	10	33.1	30.0	21.8	48
2	2	29.1	72.6	60.3	12
	3	17.4	44.7	45	12
	4	20.3	36.1	32.8	48
	5	26.9	39.3	35.7	12
	6	23.1	29.2	26.5	12
3	2	19.5	54.2	35.1	12
	3	9.27	19.9	37.3	12
4	2	18.3	51.1	56.5	12
	3	18.3	39.3	43.4	12

Table 2 Masses of reactants (m) and reaction conditions (reaction time, t) for the synthesis of [C$_n$mim][C$_k$SO$_3$] ionic liquids

		m/g					
k	n	Ester $C_kSO_3C_n$	mim	T/°C	t/h	Yield (%)	Product
1	1	25.0	17.8	0	1	97	White solid
	2	25.0	16.8	50	72	91	Pale yellow liquid
	3	24.3	13.8	70	96	94	Pale yellow liquid
	4	35.0	18.0	70	50	86	White crystals
	5	41.9	19.7	70	72	86	White solid
	6	20.0	8.7	70	72	67	Pale yellow liquid
	8	23.8	8.9	70	72	82	Pale yellow liquid
	10	27.8	9.6	70	96	85	White solid
2	2	7.0	4.0	50	48	87	Pale yellow liquid
	3	24.0	14.9	60	72	90	Pale yellow liquid
	4	26.9	12.7	50	72	84	White solid
	5	21.5	9.3	50	72	52	White solid
	6	25.0	10.1	50	72	55	White solid
3	2	26.8	13.7	50	48	42	Yellow liquid
	3	13.7	6.8	70	72	71	White solid
4	2	36.6	17.2	50	72	70	Yellow liquid
	3	24.3	10.5	50	72	68	Yellow liquid

1,3-Dimethylimidazolium methanesulfonate. Methyl methanesulfonate (25 g, 1.05 mol eq) dissolved in ethyl ethanoate (50 cm^3) was placed in a round-bottomed flask (500 cm^3) and stirred vigorously. The mixture was cooled in an ice-bath, and 1-methylimidazole (17.8 g, 1 mol eq.) dissolved in ethyl ethanoate (50 cm^3) was added dropwise using a pressure-equalising dropping funnel. Upon addition, a strongly exothermic reaction was observed. The mixture was stirred for 8 h; subsequently, the crude solid product was collected by filtration, washed with ethyl ethanoate (4 × 50 cm^3) in order to remove unreacted reagents, and the remaining solvent was removed under reduced pressure using a rotary evaporator (60 °C, 1 h). The product was a white solid.

1-Ethyl-3-methylimidazolium hexanesulfonate. Sodium hexanesulfonate (10 g, 1.0 mol eq.) and 1-ethyl-3-methylimidazolium chloride (7.8 g, 1.0 mol eq.) were dissolved separately in methanol (150 and 40 cm^3, respectively). The solutions were combined in a round-bottomed flask (500 cm^3) and stirred for 5 d. Then, the methanol was removed under reduced pressure using a rotary evaporator (25 °C, 1 h). Subsequently, propanone (100 cm^3) was added to the mixture in order to precipitate sodium chloride; the precipitate was removed by filtration, and the propanone was removed under reduced pressure to yield a yellow liquid.

Prior to use, all synthesised ionic liquid samples were thoroughly degassed and dried to remove any small traces of volatile compounds by applying a vacuum (*ca.* 0.1 Pa) at moderate temperatures (60–80 °C) for at least 24 h.

Results and discussion

Synthetic procedures

The general procedure, used to synthesise most of the ionic liquids, provided an efficient and chloride-ion-free synthetic route. The yield for ionic liquids was typically better than 70%, and in one case approached 97%. The reaction was essentially quantitative, with purification being the yield-reducing step.

In the case of 1,3-dimethylimidazolium methanesulfonate and 1-ethyl-3-methylimidazolium methanesulfonate, the corresponding esters were readily available, so step (i) was omitted. Moreover, the reaction of the synthesis of 1,3-dimethylimidazolium methanesulfonate is very exothermic, hence the procedure for step (ii) was modified and described separately.

In the case of 1-ethyl-3-methylimidazolium hexanesulfonate, an alternative synthetic route was used due to the high cost of the starting material.

Nuclear magnetic resonance spectroscopy

All the intermediate esters of the general formula $C_kSO_3C_n$ were prepared and purified as described above. As these were key reagents in the syntheses of the alkylsulfonate ionic liquids, it was important to establish that no other esters were present. ^{1}H NMR spectroscopy established the absence of any other esters or alcohols.

^{1}H and ^{13}C NMR spectra of the [$C_n$mim][C_kSO_3] ionic liquids showed no major impurities in the untreated, original samples, except for the presence of residual water (detected independently by Karl Fischer analysis); typical spectra are shown in Fig. 1S of the ESI.† ^{1}H NMR signals obtained for the ionic liquids are also given in Table 1S of the ESI,† along with ^{13}C NMR signals listed in Table 2S:† assignments are in accordance with the literature, including those reported for similar compounds.[5,10]

Mass spectrometry

All the ionic liquids prepared were examined by electrospray mass spectrometry (MS), in ethanenitrile. Only one peak was observed for each ionic liquid in positive mode or in negative mode, corresponding to cation or anion in each case (see Table 3). Accurate mass spectrometry confirmed the identity of each of the ions within the experimental error of the technique.

Melting point measurements

The melting points (T_m) measured for the ionic liquids studied are reported in Table 4. A typical example of a DSC curve is presented in Fig. 3.

The majority of the ionic liquids studied have melting temperatures above the ambient, except in the cases of [C_2mim][C_3SO_3], [C_2mim][C_6SO_3] and [C_3mim][C_2SO_3] that have melting points below 20 °C. Three other ionic liquids—[C_2mim][C_1SO_3], [C_2mim][C_2SO_3] and [C_3mim][C_4SO_3]—have melting points close to 30 °C and all other 1-alkyl-3-methylimidazolium alkanesulfonate ionic liquids melt at higher temperatures, with a maximum of 91 °C for [C_1mim][C_1SO_3].

Fig. 4 shows a dependency of the melting point upon the cationic chain length, but there are not enough data to determine whether there is any pattern associated with anionic chain length. Similarly, it is difficult to perceive a pattern in the sparse data available for the 1-ethyl-3-methylimidazolium alkylsulfates,[7] [C_2mim][C_kSO_4], where the melting point temperature seems to vary randomly.[7,11] In contrast, the melting point temperatures of 1-alkyl-3-methylimidazolium tetrafluoroborate[12] and hexafluorophosphate[13] ionic liquids, although showing no monotonic behaviour, present a regular, easy to rationalise pattern as the size of the alkyl chain in the cation varies. The melting point temperatures of the three members of the family that had been previously studied,[5] [C_1mim][C_1SO_4], [C_4mim][C_2SO_4], and [C_4mim][C_1SO_4], compare quite well for the two first cases, but exhibit a large deviation in the last case (*cf.* Table 4).

The enthalpies of fusion are reported in Table 4. The highest value was found for [C_{10}mim][C_1SO_3] (*ca.* 38 kJ mol^{-1}), while the majority of the samples studied have enthalpies of fusion between 14 and 22 kJ mol^{-1}.

Table 3 Electrospray MS results obtained for [$C_n$mim][C_kSO_3] ionic liquids obtained for each ionic liquid in positive mode (M^+ (100) is the mass nominal value of the singular peak) or in negative mode (M^- (100) is the mass nominal value of the singular peak)

k	n	M^+ (100)	m_{calc}	m_{exptl}	Δm[a]	M^- (100)	m_{calc}	m_{exptl}	Δm[a]
1	1	97	97.0776	97.0770	0.0006	95	94.9803	94.9795	0.0008
	2	111	111.0922	111.0922	0	95	94.9803	94.9800	0.0003
	3	125	125.1079	125.1076	0.0003	95	94.9803	94.9801	0.0002
	4	139	139.1235	139.1228	0.0007	95	94.9803	94.9799	0.0004
	5	153	153.1392	153.1383	0.0009	95	94.9803	94.9796	0.0007
	6	167	167.1548	167.1499	0.0049	95	94.9803	94.9796	0.0007
	8	181	181.1829	181.1822	0.0007	95	94.9803	94.9799	0.0004
	10	223	223.2174	223.2164	0.001	95	94.9803	94.9798	0.0005
2	2	111	111.0922	111.0966	−0.0044	109	108.9959	108.9980	−0.0021
	3	125	125.1079	125.1073	0.0006	109	108.9959	108.9950	0.0009
	4	139	139.1235	139.1231	0.0004	109	108.9959	108.9953	0.0006
	5	153	153.1392	153.1389	0.0003	109	108.9959	108.9952	0.0007
	6	167	167.1548	167.1550	−0.0002	109	108.9959	108.9970	−0.0011
3	2	111	111.0922	111.0924	−0.0002	123	123.0116	123.0106	0.001
	3	125	125.1079	125.1077	0.0002	123	123.0116	123.0112	0.0004
4	2	111	111.0922	111.0922	0	137	137.0272	137.0264	0.0008
	3	125	125.1079	125.1076	0.0003	137	137.0272	137.0263	0.0009
6	2	111	111.0922	111.0921	0.0001	165	165.0585	165.0580	0.0005

[a] $\Delta m = m_{calc} - m_{exptl}$.

Table 4 Values of the melting points, T_m, and of the enthalpies of fusion, ΔH_{fus}, for the 1-alkyl-3-methylimidazolium alkylsulfonate ionic liquids, [$C_n$mim][C_kSO_3], as measured by DSC or a visual method. The temperature values obtained from DSC data were calculated using the usual melting peak tangent-intersection procedure. Values in parentheses were reported in ref. 5

	k									
	1		2		3		4		6	
n	T_m/°C	ΔH_{fus}/kJ mol^{-1}	T_m/°C	ΔH_{fus}/kJ mol^{-1}	T_m/°C	ΔH_{fus}/kJ mol^{-1}	T_m/°C	ΔH_{fus}/kJ mol^{-1}	T_m/°C	ΔH_{fus}/kJ mol^{-1}
1	91.0 (93.2)	17.5	—	—	—	—	—	—	—	—
2	30.6	16.0	26–32[a]	—	37–43[a]	—	1–7[a]	—	19.1	12.4
3	39.8	15.2	19.0	14.0	32.0	11.3	47.2	20.8	—	—
4	73.7 (52.0)	22.0	57.3 (57.0)	19.6	53.0	14.1	—	—	—	—
5	76.7	21.9	54.4	16.1	—	—	—	—	—	—
6	44–50[a]	—	65.7	16.9	—	—	—	—	—	—
8	38.4	33.9	—	—	—	—	—	—	—	—
10	57.4	38.4	—	—	—	—	—	—	—	—

[a] Temperature range of the visually determined melting point temperatures.

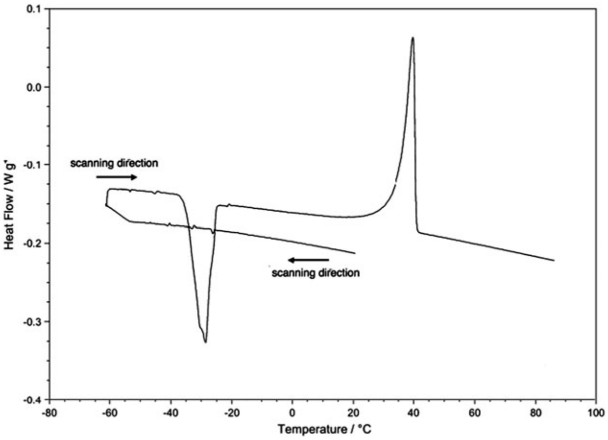

Fig. 3 A typical DSC scan for [$C_n$mim][C_kSO_3] ionic liquids; example of [C_3mim][C_1SO_3], scan speed 1 K min^{-1}.

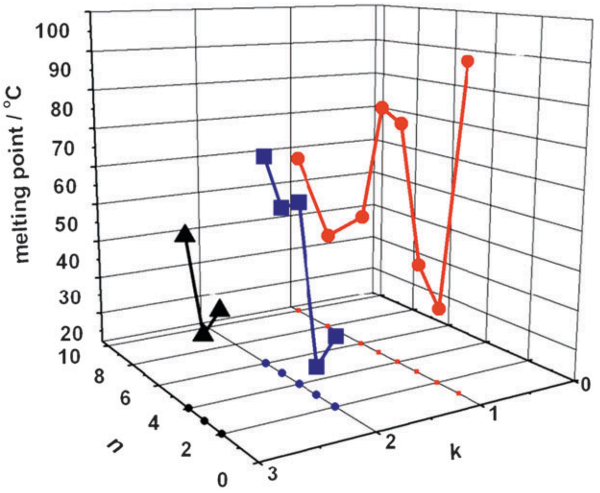

Fig. 4 Dependency of the melting point upon the cationic chain length for three series of [$C_n$mim][C_kSO_3] ionic liquids; k = 1 (circles), k = 2 (squares) or k = 3 (triangles).

Table 5 Decomposition temperatures, T_d, for [$C_n$mim][C_kSO_3], by dynamic TGA

	T_d/°C		
	k		
n	1	2	4
1	380	—	—
2	—	342	340
3	333	—	349
4	352	—	—
6	337	—	—
10	335	—	—

Thermogravimetric analysis

Decomposition temperatures (onset of weight loss in the thermogravimetric run) are reported in Table 5. A typical TGA scan is shown in Fig. 5. It should be noted, however, that these data should be treated with extreme caution. Scanning TGA significantly overestimates decomposition temperatures (by up to 150 °C),[14] but the sequence of data is reliable when the samples are run under identical conditions.

With this caveat, the ionic liquids studied have shown good thermal stability, with decomposition temperatures ranging from 330 to 380 °C. In contrast, the decomposition temperature of 1-ethyl-3-methylimidazolium ethanesulfate is significantly lower (230 °C, determined here under identical conditions). This confirms that, as expected, the ionic liquids based on alkylsulfonates are significantly more stable than those based on alkylsulfates.

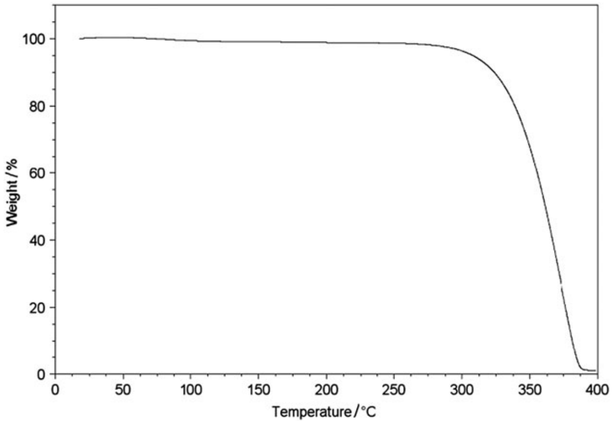

Fig. 5 A typical TGA curve for [$C_n$mim][C_kSO_3] ionic liquids; example of [C_3mim][C_1SO_3].

Density

The viscosity-corrected density measurements are reported in Table 6, along with the corresponding molar volume data, V_m, for each studied ionic liquid. The repeatability of the density measurements was better than 0.05 kg m^{-3} and the expanded uncertainty was estimated as ranging from ±0.3 kg m^{-3} to ±2 kg m^{-3} for low-viscosity and high-viscosity samples, respectively.[15] All reported density data were corrected for the effect of viscosity on density determinations with a vibrating tube densimeter, according to the empirical equation, $(\rho - \rho_{raw})/\rho_{raw} = (0.5 - 0.45\eta^{0.5}) \times 10^{-4}$, where ρ and ρ_{raw} are the corrected and measured (raw) densities, respectively, and η (mPa s) is the sample viscosity.[16] Herein, the correction can be as high as 1.7 kg m^{-3} for samples with viscosities greater than 1700 mPa s.

The temperature-dependence of the density data is fitted by a simple linear regression, and the fitting parameters are also shown in Table 6. The deviations between the fitted and experimental V_m data are smaller than 0.005%—comparable to the repeatability of the measurements—which means that a $\ln(\rho) = f(T)$ function more complex than a simple straight line is not warranted in this case (as in the case of ionic liquids in general[16–18]). The advantage of using a linear regression to fit $\ln(\rho)$ values is that the thermal expansion coefficient, α_p, for each ionic liquid will be a constant at a given pressure and it will be easy to obtain from the slope of the regression line: if $\ln(\rho) = mT + b$, then $d\ln(\rho)/dT = -\alpha_p = m$. Fig. 6 shows the values of α_p for the eight ionic liquids where density data were measured at different temperatures.

Fig. 6 shows that, although the scatter of the α_p values is much larger than that of the ρ data (the former quantity is a derived property of the latter), there is a correlation between the total number of carbon atoms in the alkyl side chain and the value of α_p.

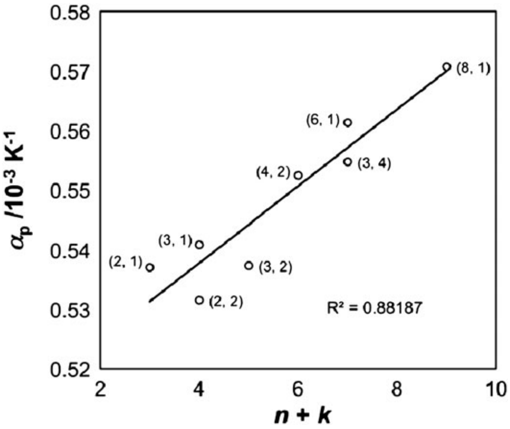

Fig. 6 Temperature-independent thermal expansion coefficient, $\alpha_p = -[\partial(\ln \rho)/\partial T]_p$, as a function of the total number of carbon atoms, $n + k$, in the alkyl side chains of $[C_n mim][C_k SO_3]$ ionic liquids, calculated from the density data obtained at atmospheric pressure. Points are identified as (n, k). The straight line represents the linear regression, $R^2 = 0.88$.

The molar volume results show a consistent trend along the series of 1-alkyl-3-methylimidazolium alkanesulfonate ionic liquids, increasing proportionally with the number of the methylene (–CH_2–) groups present in the alkyl chains of the cation and/or the anion. An extra mole of methylene groups in the alkyl chains will always increase its molar volume by the same amount, 17.06 ± 0.04 cm^3 mol^{-1} at 298.15 K, irrespective of the ionic liquid itself; this value compares favourably with a previous, multi-averaged determination of an increase of 17.2 ± 0.3 cm^3 mol^{-1} per (–CH_2–) at 298.15 K.[17,18] To the best of our knowledge, it is shown, herein, for the first time that this change is irrespective of the (–CH_2–) addition taking

Table 6 Experimental values of the density, ρ/g cm^{-3}, and molar volume, V_m, of $[C_n mim][C_k SO_3]$ ionic liquids, at temperatures T = 293.15 to 333.15 K. The δV_m values represent the difference between V_m values and molar volume data calculated using the fitting equations. In these equations, the slope is symmetrical to the temperature-independent thermal expansion coefficient, $\alpha_p = -[\partial(\ln \rho)/\partial T]_p$—see Fig. 6

		k								
		1			2			4		
n	T/K	ρ/g cm^{-3}	V_m/cm^3 mol^{-1}	δV_m/cm^3 mol^{-1}	ρ/g cm^{-3}	V_m/cm^3 mol^{-1}	δV_m/cm^3 mol^{-1}	ρ/g cm^{-3}	V_m/cm^3 mol^{-1}	δV_m/cm^3 mol^{-1}
2		$\ln(\rho) = 0.3754 - (0.5370 \times 10^{-3})\ T$			$\ln(\rho) = 0.3439 - (0.5315 \times 10^{-3})\ T$			$\ln(\rho) = 0.2982 - (0.5524 \times 10^{-3})\ T$		
	293.15	1.24347	165.879	−0.005	1.20691	182.526	0.002	1.14601	216.705	−0.002
	298.15	1.24020	166.317	0.003	1.20366	183.019	−0.006	1.14287	217.301	0.002
	313.15	1.23027	167.658	0.006	1.19419	184.470	0.008	1.13343	219.110	0.001
	333.15	1.21706	169.478	−0.003	1.18149	186.453	0.003	1.12097	221.545	−0.001
3		$\ln(\rho) = 0.3462 - (0.5408 \times 10^{-3})\ T$			$\ln(\rho) = 0.3178 - (0.5373 \times 10^{-3})\ T$			$\ln(\rho) = 0.2779 - (0.5547 \times 10^{-3})\ T$		
	293.15	—	—	—	1.17383	199.619	−0.001	1.12215	233.813	−0.009
	298.15	—	—	—	1.17071	200.152	0.003	1.11912	234.446	0.007
	313.15	1.19351	184.576	0	1.16128	201.778	−0.003	1.10984	236.407	0.005
	333.15	1.18067	186.583	0	1.14889	203.954	0.001	1.09756	239.052	−0.003
4	333.15	—	—	—	1.12170	221.401	—	—	—	—
6		$\ln(\rho) = 0.2791 - (0.5613 \times 10^{-3})\ T$								
	293.15	1.12137	233.976	−0.006	—	—	—	—	—	—
	298.15	1.11828	234.622	0.006	—	—	—	—	—	—
	313.15	1.10889	236.610	0.002	—	—	—	—	—	—
	333.15	1.09649	239.285	−0.002	—	—	—	—	—	—
8		$\ln(\rho) = 0.2489 - (0.5707 \times 10^{-3})\ T$								
	293.15	1.08499	267.678	0.005	—	—	—	—	—	—
	298.15	1.08184	268.458	−0.010	—	—	—	—	—	—
	313.15	1.07268	270.749	0.007	—	—	—	—	—	—
	333.15	1.06047	273.866	−0.002	—	—	—	—	—	—

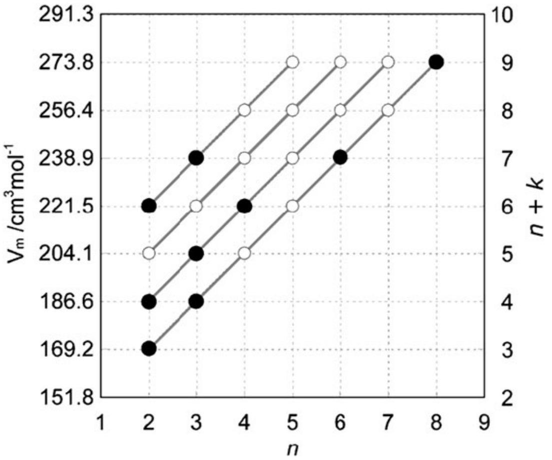

Fig. 7 Experimental molar volume of 1-alkyl-3-methylimidazolium alkylsulfonate, $[C_n\text{mim}][C_kSO_3]$, ionic liquids at 333.15 K (●) as a function of the number of carbon atoms in the alkyl chain of the cation (x-axis), n, and the total number of carbon atoms in the alkyl chains of both ions (secondary y-axis), $(n + k)$. The open dots represent other members of the 1-alkyl-3-methylimidazolium alkanesulfonate family whose density was not measured experimentally but can be estimated using the molar volume additive character within the family. The lines represent series of ionic liquids with the same number of carbon atoms in the anion, and have a slope of 17.45 cm^3 mol^{-1}, at 333.15 K.

place in the cation or the anion. Fig. 7 depicts such behaviour, with the experimental molar volume points (closed circles) superimposed in a regular grid (open circles) built taking into account only the number of methylene groups in the alkyl chains of the cation (x-axis) and the total number of methylene groups of the ionic liquid (secondary y-axis). As stated above, the nature of the family of ionic liquids studied in this work, where the size of the alkyl chains can be varied both in the anion and in the cation, implies that it can be ordered not in a simple 'row' but in a 'matrix'. This fact is clearly denoted in Fig. 7 by the above-mentioned regular grid of white points. The observation that all experimentally determined molar volumes fit that grid, with deviations always smaller than 0.2%, constitutes a proof of the additive character of the molar volume within this particular family of ionic liquids.

Table 7 Effective molar volumes of different constituent parts of 1-alkyl-3-methylimidazolium alkanesulfonates: extension of previously established contribution schemes for the estimation of the molar volume of ionic liquids. The molar volume of any ionic liquid, $[C_n\text{mim}][C_kSO_3]$, is estimated by adding the molar volumes of $(n + k)$ $(–CH_2–)$ groups to the molar volumes of $[C_0\text{mim}]^+$ and $[C_0SO_3]^-$ (values for T = 298.15 K)

	V_m/cm^3 mol^{-1}			
	Rebelo *et al.*[22]	Ye and Shreeve[19]	Jacquemin *et al.*[20]	This work
$[C_0\text{mim}]^+$	64.8[a]	75.9[b]	66.0[a]	66.0[a]
$[C_0SO_3]^-$	—	—	—	48.9
$–CH_2–$	17.2	16.9	17.1	17.06

[a] Scheme based on the hypothesis that in $[PF_6]^-$-based ionic liquids the contribution of $[PF_6]^-$ to the molar volume is 73.7 cm^3 mol^{-1}.
[b] Scheme based on a contribution of $[PF_6]^-$ equal to 64.4 cm^3 mol^{-1}.

The idea of estimating the density along a family of ionic liquids using the additive character of V_m *via* the sum of effective ion volumes was first proposed by Rebelo *et al.*[18] and further refined by other authors[19–21] who devised empirical group contribution methods (see Table 7). The present data confirm the general validity of those methods and extend their scope: (i) alkanesulfonate-based ionic liquids were added to the list of compounds whose density can be estimated—at 298.15 K, the group, $[C_0SO_3]^-$, contributes with 48.9 cm^3 mol^{-1} for those methods[17,20] (to be compared with $[C_0SO_4]^-$ = 57.0 cm^3 mol^{-1}—taken as the difference between the molar volume of $[C_2SO_4]^-$ and the volume of two methylene groups)[20,22] where the contribution of the anion $[PF_6]^-$ was postulated as 73.7 cm^3 mol^{-1}; and (ii) most importantly, it was shown that these methods work not only by regularly varying the structure of one of the ions constituting the ionic liquid (along 'row-like' families of ionic liquids) but also by simultaneously changing the structure of the two ions ('matrix-like' ionic liquid families like in the 1-alkyl-3-methylimidazolium alkanesulfonate series).

The recent discovery that ionic liquids can be understood as nano-segregated fluids,[23] composed of a polar network permeated by non-polar islands or domains, can help one to understand, from a molecular point of view, the fact that an added methylene group always contributes to an increase in the molar volume of the ionic liquid of *ca.* 17 cm^3 mol^{-1}, irrespective of the nature of the ionic liquid: such nano-segregation implies that when a methylene group is added to an existing alkyl side chain it will tend to be positioned near other alkyl side chains, *i.e.* a molecular environment similar to that of linear alkanes. In the series of linear alkanes (from hexane to decane at 298 K and 1 atm), the molar volume also increases in a monotonic and regular manner, with each extra $–CH_2–$ group adding 16 cm^3 mol^{-1} to the molar volume of the previous member of the series (deviations from this pattern are smaller than 0.2%).[24]

Viscosity

It was observed that the ionic liquid samples were highly hygroscopic and, even when all the appropriate precautions were taken, water uptake by the samples could be detected. This effect was evaluated by measuring the viscosity of the ionic liquid samples at regular time intervals, which showed a decrease in viscosity of less than 10% after 10 h, at 295 to 360 K. Thus, the overall uncertainty of the present viscosity measurements can be estimated as $<5\%$.

The results obtained for the viscosity of the ionic liquid samples are included in Table 8. The values range from 17 mPa s for $[C_2\text{mim}][C_2SO_3]$ at 356 K to 1055 mPa s for $[C_2\text{mim}][C_4SO_3]$ at 296 K. These values are similar to those found for alkylsulfate-based ionic liquids, or for $[C_4\text{mim}][PF_6]$, as can be seen in Fig. 8.

The experimental viscosities were correlated with temperature using both an Arrhenius-like expression, eqn (1), and a Vogel–Fulcher–Tamman (VFT) equation, eqn (2):[26]

$$\eta = \eta_\infty \exp(-E_a/RT) \tag{1}$$

$$\eta = AT^{0.5}\exp(B/(T - T_0)) \tag{2}$$

Table 8 Experimental values of the viscosity for a series of [$C_n$mim][C_kSO_3] ionic liquids

	k											
	1				2				4			
n	*T*/K	η/mPa s	Dev (1)[a] (%)	Dev (2)[b] (%)	*T*/K	η/mPa s	Dev (1)[a] (%)	Dev (2)[b] (%)	*T*/K	η/mPa s	Dev (1)[a] (%)	Dev (2)[b] (%)
2	295.06	184.73	14.30	0.03	296.11	233.61	11.09	0.05	296.37	531.41	15.28	0.03
	302.57	113.87	0.50	−0.10	302.61	153.51	0.86	−0.25	302.53	328.18	1.99	−0.16
	312.07	68.24	−7.87	−0.32	312.08	91.71	−5.87	0.41	312.00	175.52	−7.74	0.28
	321.51	45.45	−8.71	1.10	321.58	58.53	−8.45	−0.19	321.44	103.50	−10.99	−0.08
	330.97	31.53	−7.78	0.09	331.02	40.36	−6.34	0.35	330.93	66.57	−8.66	0.54
	345.13	20.25	−0.01	−0.38	345.17	25.14	1.24	0.39	345.05	37.95	−0.52	−0.48
	359.22	14.07	12.25	−1.61	357.08	17.65	9.22	−1.76	359.25	23.88	13.98	−1.75
3	302.55	236.95	10.90	0.16	295.29	566.08	13.45	−0.11	295.92	1054.72	19.52	0.67
	312.01	129.09	−2.05	−0.42	302.51	329.97	1.25	0.34	302.52	562.62	−2.10	−3.50
	321.52	77.49	−7.13	−0.15	312.02	179.24	−6.47	0.66	312.00	293.88	−8.24	2.99
	331.00	50.17	−7.61	0.28	321.45	105.48	−9.65	−0.72	321.44	166.49	−10.12	5.68
	345.14	29.31	−1.99	1.51	330.89	67.01	−8.40	−1.70	330.95	99.94	−9.24	5.33
	359.25	18.92	9.47	2.97	345.06	37.95	−0.20	−2.52	345.14	53.03	−0.77	4.56
4	—	—	—	—	359.22	23.48	12.70	−4.41	359.25	31.72	15.06	3.72
	—	—	—	—	326.32	100.89	1.67	0.08	—	—	—	—
	—	—	—	—	335.79	64.49	−2.21	−0.49	—	—	—	—
	—	—	—	—	345.27	44.50	−0.69	0.77	—	—	—	—
	—	—	—	—	354.66	31.58	1.27	−0.26	—	—	—	—
10	326.17	248.52	1.05	−0.38	—	—	—	—	—	—	—	—
	335.68	149.88	0.01	2.28	—	—	—	—	—	—	—	—
	345.12	91.05	−3.29	−2.27	—	—	—	—	—	—	—	—
	354.56	62.01	2.32	−1.42	—	—	—	—	—	—	—	—

[a] Dev(1) = $(\eta_i^{\text{exp}} - \eta_i^{\text{cal (eqn 1)}})/\eta_i^{\text{cal (eqn 1)}}$. [b] Dev(2) = $(\eta_i^{\text{exp}} - \eta_i^{\text{cal (eqn 2)}})/\eta_i^{\text{cal (eqn 2)}}$.

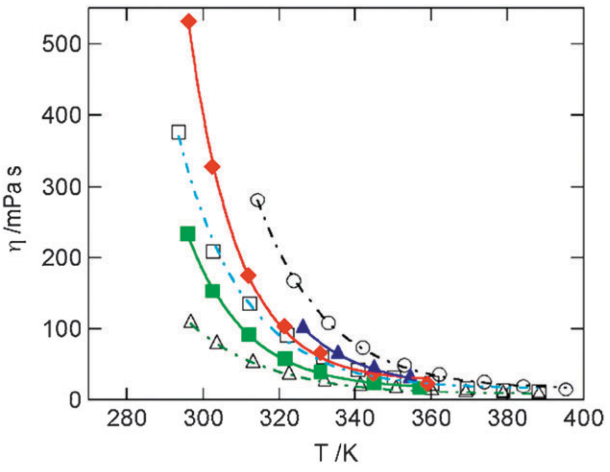

Fig. 8 Experimental viscosities as a function of temperature: (○), [C_4mim][C_8SO_4];[25] (□), [C_4mim][PF_6];[9] (Δ), [C_2mim][C_2SO_4];[9] (◆), [C_2mim][C_4SO_3]; (▲), [C_4mim][C_2SO_3]; (■), [C_2mim][C_2SO_3].

where η_∞ is the viscosity at infinite temperature and E_a is the viscosity activation energy, two characteristic parameters adjusted from experimental data as a function of temperature. *A*, *B* and T_0 in eqn (2) are three adjustable parameters. Table 9 lists the parameters for the ionic liquids studied in the present case, together with the standard relative deviations of the fits.

The viscosity of alkanesulfonate based ionic liquids decreases rapidly with increasing temperature. For example, for [C_3mim][C_4SO_3], one of the more viscous ionic liquids studied in this work, the viscosity decreases one order of magnitude when the temperature changes from 296 K to 330 K. This behaviour is also found for [C_{10}mim][C_1SO_3], a solid at room temperature, for which the viscosity decreases by a factor of 4 when increasing the temperature from 326 K to 355 K.

In the family of alkylimidazolium alkanesulfonate ionic liquids, it is observed that the viscosity of the ionic liquid increases, as expected, when the alkyl chain increases, either in the cation, or in the anion, or in both. This effect can be observed in Fig. 9, where the increase in viscosity is represented, at 323 K, as a function of the number of carbon atoms in the alkyl chains (*n* or *k*).

An increase of the viscosity by 25 to 50 mPa s is observed (see Fig. 9) with the increase of one extra carbon atom in the alkyl side chain of the 1-alkyl-3-methylimidazolium cation. A similar trend, although smaller, has also been observed by Tokuda *et al.*[27] for the viscosity of 1-alkyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}-amide ionic liquids.

The size of the alkyl side chain in the alkanesulfonate anion also influences the viscosity of the ionic liquids studied in this work. The viscosity increases by (13 ± 1) mPa s and by (22 ± 0.5) mPa s for each extra carbon atom in the alkyl chain of the anion for [C_2mim]$^+$-based ionic liquids and [C_3mim]$^+$-based ionic liquids, respectively. This behaviour confirms that, although the high-electrostatic interactions between ions determine the characteristic physicochemical properties of ionic liquids, dispersive, van der Waals-type forces also play an important role and determine the way the viscosity changes with the size of the alkyl side chain. This suggests that the formation of non-polar molecular domains, dominated by van der Waals-type molecular interactions, may determine the variation of viscosity in a family of ionic liquids. However, their impact in equilibrium (*e.g.* molar volume) *versus* transport (*e.g.* viscosity) properties is different. While (ideal) additive behaviour is observed for the former, a more complex response is found for the latter.

Table 9 Correlation parameters of the Arrhenius-like equation, eqn (1), and of the VFT equation, eqn (2), with the deviations of the fit $\sigma_r{}^a$ for the viscosity of $[C_n\text{mim}][C_kSO_3]$ as a function of temperature, determined from experimental values in the range $T = 295$ to $T = 360$ K

		Arrhenius-type equation [eqn (1)]			VFT equation [eqn (2)]			
n	k	$\eta_\infty/10^{-6}$ mPa s	$-E_a$/kJ mol^{-1}	σ_r	$A/10^{-3}$ mPa s K$^{1/2}$	B/K	T_0/K	σ_r
2	1	97.92	35.12	0.11	19.68	555.0	207.0	0.01
	2	62.54	37.00	0.08	11.71	711.5	195.2	0.01
	4	9.859	43.52	0.12	11.82	728.8	203.7	0.01
3	1	25.69	40.08	0.09	6.119	837.9	193.8	0.02
	2	8.869	43.81	0.10	7.613	849.7	193.8	0.03
	4	2.554	48.37	0.13	8.506	812.2	204.4	0.05
4	2	50.72	39.30	0.02	7.543	843.7	198.6	0.01
10	1	6.227	47.44	0.02	9.847	844.5	209.6	0.04

[a] Deviation defined as: $\sigma_r = \left(\frac{\sum_i \left[\left(\eta_i^{\text{exp}} - \eta_i^{\text{calc}}\right)/\eta_i^{\text{calc}}\right]^2}{n-\nu}\right)^{0.5}$ where n is the number of experimental points and ν the number of adjustable parameters.

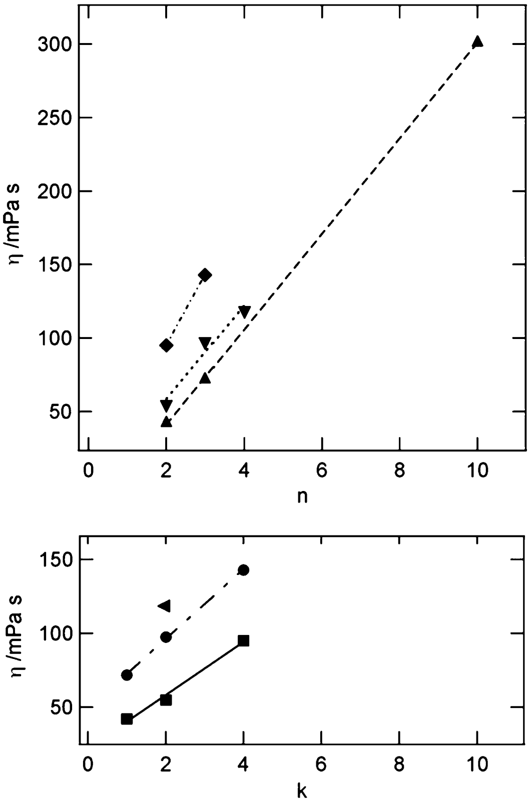

Fig. 9 Variation of the viscosity at 323 K with the number of carbon atoms in the alkyl chains in the cation, n, and in the anion, k, forming the ionic liquid. Top: variation of viscosity with the number of carbon atoms in the alkyl side chain of the 1-alkyl-3-methylimidazolium cation, n. ▲, $[C_n\text{mim}][C_1SO_3]$; ▼, $[C_n\text{mim}][C_2SO_3]$; ◆, $[C_n\text{mim}][C_3SO_3]$. Bottom: variation of viscosity with the number of carbon atoms in the alkyl chain of the sulfonate anion, k. ■, $[C_2\text{mim}][C_kSO_3]$; ●, $[C_3\text{mim}][C_kSO_3]$; ◀, $[C_4\text{mim}][C_kSO_3]$.

Conclusions

A matrix of 1-alkyl-3-methylimidazolium alkanesulfonate ionic liquids, $[C_n\text{mim}][C_kSO_3]$, formed by variations of the alkyl chain lengths in the cation and in the anion (n = 1–6, 8, or 10; k = 1–4, or 6), was prepared and characterised. Viscosities, densities, melting points and decomposition temperatures were determined, and the results were compared with the available data for other ionic liquid series (*e.g.* $[C_n\text{mim}][BF_4]$, $[C_n\text{mim}][PF_6]$, $[C_n\text{mim}][NTf_2]$ and $[C_n\text{mim}][C_kSO_4]$). Melting points of the alkanesulfonates showed a dependency upon the cationic chain length, but no pattern was found for the enthalpies of fusion. Decomposition temperatures of the $[C_n\text{mim}][C_kSO_3]$ series were found above 300 °C (dynamic TGA scans). Densities of the examined ionic liquids were correlated to the sum of the carbons in the alkyl chains, both in the anion and in the cation ($n + k$); it was shown that, irrespective of position, the additional methylene groups increase the molar volume of the ionic liquids by the same value. Patterns in viscosity changes observed for the $[C_n\text{mim}][C_kSO_3]$ series corresponded to findings for other homologous series, *e.g.* hexafluorophosphates, and can be correlated with the Vogel–Fulcher–Tamman (VFT) model. Whereas the density and the viscosity show similar behaviour in both families (alkanesulfonates and alkanesulfates), the thermal stability of alkanesulfonates shows a much better performance.

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