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Effect of sulfonate-based anions on the physicochemical properties of 1-alkyl-3-propanenitrile imidazolium ionic liquids

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In this paper, the physicochemical properties of a new series of ionic liquids (ILs) based on nitrile-functionalised imidazolium cations ($[C_2CN C_n im]^+$) with sulfonate-based anions were studied. The ILs were prepared by reacting imidazole with acrylonitrile, followed by butyl-and decyl bromide. The anions of the resulting bromide salts exchanged by metathesis to dioctylsulfosuccinate (DOSS), dodecylsulfate (DDS), benzenesulfonate (BS) and trifluoromethanesulfonate (TFMS). The densities of these ILs are lower compared to the those of other reported nitrile-functionalised ILs, while on the other hand, the viscosities of the ILs are higher due to the effects of the large anions and the long alkyl chain of the cations.

Introduction

The term ionic liquids (ILs) is the common name given to organic salts that have melting points below 100 °C and negligible vapor pressure.¹ ILs are exclusively composed of organic cations and inorganic or organic anions, they vary in size and can be either hydrophilic or hydrophobic.^{2,3} The unique combination of their inherent physical and chemical properties, namely low melting points, high thermal stability, liquidity over a wide temperature range, negligible vapor pressures, low flammability, highly solvating capacity for both polar and non-polar compounds, high electrical conductivity,^{3,4} and easy recycling, mean these compounds attract a considerable amount of attention in many fields.⁵ Their unique properties as a designer solvent receive increasing and continuing attention in many important areas of research and commercial applications, such as absorption media for gas separations, solvents for reactions, heat transfer fluids, separating agents in extractive distillation, biomass processing, as the working fluid in a variety of electrochemical applications (batteries, capacitors, solar cells, etc.),⁶ as lubricants⁷ and in biocatalysts with great advantages.8

The combination of cations and anions, the type of functional groups and the alkyl chain length has a prominent influence on the chemical and physical properties of ILs. The term task-specific or functionalised ILs was introduced in order to illustrate ILs with functional groups that provide particular properties.⁹

Nitrile-functionalised ILs are a relatively new class of ILs with special properties and potential applications in many areas. These include reaction media, ligands for catalytic reactions, electrolytes for lithium batteries, dye-sensitised solar cells,^{10–12} and also in the fields of organic synthesis, extraction and dissolution.¹³ In fact, it appears that an advantage of nitrile-functionalised ILs over the conventional ILs is that they provide more opportunities to fine-tune physical and chemical properties by modifying the hydrogen bonding network architecture of the IL.¹⁴

To facilitate the molecular design of nitrile-functionalised ILs, a fundamental understanding of the effects of alkyl chain length, type of functional group and anion choice on the IL's properties is essential. Although nitrile-functionalised ILs with short and long alkyl chain lengths have been synthesised, the effect of anions with different functional groups and alkyl chain lengths in these ILs with cationic species incorporating different alkyl chains still needs to be explored.^{14,15} The cation and anion structures can certainly influence the physical and chemical properties such as viscosity, density, refractive index and thermal stability, as well as interaction with dissolved molecules.¹²

Many researchers have synthesised the imidazolium-based nitrile-functionalised ILs with different lengths of the alkyl chain unit linking the imidazolium ring and the nitrile group.^{12,15} Imidazolium-based nitrile-functionalised ILs with long alkyl chains attached to the N-3 of the imidazolium ring have recently been synthesised by our group.¹⁴ This present study involves the synthesis of a new series of 1-alkyl-3-propanenitrile imidazolium ionic liquids incorporating different sulfonate-based anions, such as dioctylsulfosuccinate (DOSS), dodecylsulfate (DDS), benzenesulfonate (BS), and trifluoromethanesulfonate (TFMS). They are synthesised by reacting

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imidazole with acrylonitrile and then reacting the product with 1-bromoalkane. After the reaction was completed, a metathesis reaction was carried out using (DOSS), (DDS), (BS) and (TFMS) anions. The structure of the products was verified with ¹H and ¹³C-NMR, FTIR and elemental analysis. Despite their importance and interest in their commercial applications, a detailed study on the physicochemical properties of these ionic liquids has not been performed. In the present work, the important properties, namely density, viscosity, refractive index and thermal stability for the ILs were measured.

Results and discussion

The following scheme shows the route taken for this synthesis (Scheme 1).

The ¹H NMR spectra showed that the C-2 peak of the imidazolium ring of these ionic liquids lies between 7.77–9.95 ppm. Sulfonate-based anions that have strong electron with-drawing groups, such as trifluoromethyl and carbonyl, cause the C-2 of the imidazolium cation to resonate downfield compared to benzene sulfonate and dodecylsulfonate.

The main feature in the FTIR spectra was the weak absorption of the CN group in the range 2245–2265 cm⁻¹ (Fig. 1). The larger the sulfonate-based anions, the weaker the CN peak. Characteristic absorption peaks for the $-SO_3^-$ group in the regions 1190–1249 cm⁻¹ and 1029–1163 cm⁻¹ were observed.





Fig. 1 FTIR-ATR spectra of the ionic liquids [C₂CN C_nim]X.

The effects of impurities (especially water and halide) on the physical properties of ILs are well known. The presence of water may have a rather dramatic effect on density, viscosity, refractive index and thermal stability. The water content and bromide contents (as a mass fraction) of the synthesised ILs were determined and are in the ranges 170–235 ppm (water) and 70–103 ppm (bromide).

Table 1 shows the density, viscosity and refractive indices of the synthesised ILs at 298.15 K. The measured densities are low when compared to those of analogous nitrile-functionalised ILs with different anions, as reported by Zhao *et al.*¹⁵ The densities of [C₂CN Mim]BF₄, [C₃CN Mim]BF₄ and [C₄CN Mim]Cl are 2.15, 1.87 and 1.61 g cm⁻³, respectively. The densities of the synthesised ILs are lower compared to those of the pyrrolidinium-based nitrile-functionalised ILs, for 1-cyanoalkyl-1-methylpyrrolidinium bistriflimide ([C₁C_{*n*CN}Pyr]-[NTf₂], n = 1, 2, 3, 5), the densities are in the range 1.157–1.435 g cm⁻³.¹⁶

The viscosities of these nitrile-functionalised ILs with sulfonate anions are much higher than $[C_3CN Mim]BF_4$ where the reported viscosity is 352 mPa s.¹⁵ The viscosities of the

Table 1 Density^{*a*}, ρ ; viscosity^{*a*}, η ; refractive index^{*a*}, n_D ; start temperature, T_s and decomposition temperature T_d for the synthesised RTILs

Ionic liquids	$ ho/{ m g~cm^{-3}}$	η/mPa s	<i>n</i> _D	$T_{\rm s}/^{\circ}{ m C}$	$T_{\rm d}/^{\circ}{ m C}$
[C ₂ CN Bim]DOSS	1.1105	12006	1.4805	291	307
C ₂ CN Bim DDS	1.1119	7875	1.4880	279	297
C ₂ CN Bim]BS	1.2368	2352	1.5329	298	312
C ₂ CN Bim]TFMS	1.3324	719	1.5324	314	328
[C ₂ CN Dim]DOSS	1.0358	31 0 28	1.4761	245	261
[C ₂ CN Dim]DDS	1.0666	26863	1.4745	235	246
^a Measured at 298.1	5 K.				

Table 2 Molecular volume $V_{\rm m}$, standard entropy S^0 and lattice energy $U_{\rm POT}$ of the [C₂CN C_nim]X ILs at 298.15 K

Ionic liquids	$V_{\rm m}~({\rm cm}^3)$	S^0 (J K ⁻¹ mol ⁻¹)	$U_{\rm POT}/{\rm kJ}~{\rm mol}^{-1}$
C ₂ CN Bim]DOSS	$\begin{array}{c} 8.98 \times 10^{-22} \\ 6.64 \times 10^{-22} \\ 4.52 \times 10^{-22} \\ 4.08 \times 10^{-22} \\ 1.10 \times 10^{-21} \\ 8.23 \times 10^{-22} \end{array}$	1149.41	347
[C ₂ CN Bim]DDS		857.26	373
[C ₂ CN Bim]BS		592.55	410
[C ₂ CN Bim]TFMS		538.00	421
[C ₂ CN Dim]DOSS		1398.36	332
[C ₂ CN Dim]DDS		1055.74	355

synthesised ILs are higher compared to the other nitrilefunctionalised ILs (for $[C_1C_{nCN}Pyr][NTf_2]$ (n = 1, 2, 3, 5); the viscosities are in the range 345-540 cP, as reported by Nockeman and coworkers.¹⁶ The differences in these two properties can be explained by anion size and cation chain length. The lower densities when compared to the other nitrilefunctionalised ILs are due to the presence of larger anions and more and longer alkyl chains in the cations (butyl and decyl). This causes a bigger free volume that decreases the density. Also, the presence of more -CH₂- functions reduces the overall density; this is also the same for large phosphonium ILs. The increased volumes of the anions here (trifluoromethanesulfonate excepted) lead to higher viscosities through reductions in ion mobility.¹⁷ In addition, the high viscosity can also be ascribed to increased electrostatic interactions between the cation and anion. The [C₂CN Dim]DOSS IL showed the lowest density and the highest viscosity since it possesses the largest anions, while [C₂CN Bim]TFMS showed the highest density values and the lowest viscosity.

The refractive index is related to the excess molar refraction, which is used in the least squares energy relationships (LSERs) as a predictor of solute distribution.¹⁸ The refractive index values of the synthesised ILs are in the range (1.47334–1.53939), and the values are in good agreement with those reported for other imidazolium-based nitrile-functionalised ILs; for [C₃CN Mim]-NTf₂, [C₃CN Mim]BF₄, [C₂CN Bim]Br and [C₂CN Oim]Br these are 1.4398, 1.4349, 1.54540 and 1.51473,^{12,14} respectively. The refractive indices of these nitrile-functionalised ILs with sulfonate anions are much higher compared to [C₁C_{nCN}Pyr][Tf₂N], where the reported refractive indices are in the range 1.4305–1.4365.¹⁶ The refractive index values are found to increase after the incorporation of a nitrile group, which may be due to the high electron mobility around the nitrile group.¹²

The start temperatures for weight loss (T_s) and decomposition temperatures (T_d) of the ILs, measured by TGA, are presented in Table 1. The T_d of ILs in this study are higher compared to the other common ionic liquids.¹⁴ Also, the decomposition temperatures of the synthesised ILs are high compared with that reported for [C₃CN Mim]Cl of 254.9 °C,¹⁴ as a result of replacing the basic, reactive chloride with more stable anions. The thermal stability of the trifluoromethanesulfonatecontaining IL is the highest due to the extremely stable anion. The thermal stability is also affected by the size of the alkyl chain of the cation on the nitrile group, the decomposition temperature decreases as the alkyl chain increases. The thermal stability of the ILs with DOSS, DDS, BS and TFMS anions were high in comparison with the corresponding ILs with the bromide anion (T_d of [C₂CN Bim]Br and [C₂CN Dim]Br are 251 °C and 238 °C, respectively).14

The molecular volume $(V_{\rm m})$ is the sum of the anion volume and cation volume. $V_{\rm m}$ was calculated for the ILs at 298.15 K and atmospheric pressure using the following equation:^{19,20}

$$V_{\rm m} = M/(N_{\rm A}\rho) \tag{1}$$

where *M* is the molecular weight in g mol⁻¹, N_A is Avogadro's number in mol⁻¹, ρ is the density in g cm⁻³ and V_m is molecular volume in cm³. The values of V_m are listed in Table 2.

The standard entropy for these ionic liquids was estimated as suggested by Glasser and Jenkins:²¹

$$S^0 = 1246.5 (V_{\rm m}) + 29.5$$
 (2)

where S^0 is the standard entropy at 298.15 K in J K⁻¹ mol⁻¹ and V_m is the molecular volume in nm³. The standard entropies estimated are listed in Table 2. The results show higher values compared with the other ILs, for [C_nMim]alaninate and [C_nMim]glycinate; where n = 2-6, the standard entropy ranges from 396.9–535.8 J K⁻¹ mol⁻¹ and from 360.2–498.8 J K⁻¹ mol⁻¹ respectively.^{20,22}

The lattice energy of an IL is the surface excess energy, which is reliant on the interaction energy between ions. The low lattice energy is the underlying reason for forming the IL at room temperature. Lattice energies of ionic liquids were estimated according to Glasser theory²³ using the following equation:

$$U_{\rm POT} + 1981.2(\rho/M)^{1/3} + 103.8$$
 (3)

where U_{POT} is the lattice energy in kJ mol⁻¹. The results presented in Table 2 show that lattice energies of ILs are much less than that of inorganic fused salts; the minimal lattice energy (U_{POT}) among alkali chlorides is 602.5 kJ mol^{-1.20} The results indicate that the lattice energies for the nitrilefunctionalised ILs are lower compared with that of the other ILs (for [C_n Mim]alaninate and [C_n Mim]glycinate (where n = 2-6), ranging from 421–456 and 429–469 kJ mol⁻¹, respectively.²²

The values of the glass transition temperatures (T_{a}) , melting temperatures (T_m) and cold crystallisation temperatures (T_c) were investigated. The glass transition temperature is the midpoint of a small heat capacity change on heating from the amorphous glass state to a liquid state. The melting point is the onset of an endothermic peak on heating. The cold crystallisation temperature is the onset of an exothermic peak on heating from a subcooled liquid state to a crystalline solid state.²⁴ The T_g of [C₂CN Bim]DOSS, [C₂CN Dim]DOSS, [C₂CN Bim]DDS and [C₂CN Dim]DDS ILs are -56.92, -55.59, -60.63 and -51.50 °C, respectively. [C2CN Bim]DDS and [C₂CN Dim]DDS showed a $T_{\rm m}$ of 9.00 and -22.95 °C, respectively, whilst the T_c was 6.24 and -25.65 °C, respectively When these two ILs were subjected to heating and cooling of up to 100 °C, there was nothing else happening, as observed from the DSC results. A significant change in the phase change behaviour occurred when the alkyl chain length was increased for the dodecylsulfate anions. This led to weaker Coulombic interactions in the crystal lattice, poor packing of the ions, and a decrease in the melting temperatures. In addition, these ILs did not show any liquid-crystalline phase, compared to many

1-alkyl-3-methylimidazolium salts that also have twelve carbons atoms in an alkyl chain.²⁵⁻²⁷

Conclusion

In the current work, novel ILs containing imidazolium-based cations incorporating a nitrile functionality $[C_2CNC_n im]$ and sulfonate-based anions (DOSS, DDS, BS and TFMS) were synthesised. The ILs show a lower density and a higher viscosity and higher thermal stability compared with other nitrile-functionalised ILs. Moreover, these ILs have a low lattice energy and a high standard entropy compared with the other ILs.

Experimental methods

Materials

The CAS number, source and grades of the chemicals that were used for synthesis are: imidazole (288-32-4, Aldrich 99%), acrylonitrile (107-13-1, Aldrich 99%), methanol, anhydrous (67-56-1, Sigma-Aldrich 99.8%), 1-bromobutane (109-65-9, Merck 98%), 1-bromodecane (112-29-8, Aldrich 98%), ethyl acetate, anhydrous (141-78-6, Sigma-Aldrich 99.8%), sodium dioctylsulfosuccinate (577-11-7, Aldrich 98%), sodium dodecyl sulfate (151-21-3, Sigma-Aldrich 99%), sodium benzenesulfonate (515-42-4, Aldrich 97%), sodium trifluoromethanesulfonate (2926-30-9, Aldrich 98%), diethylether (Sigma-Aldrich 99%) and acetone (Sigma-Aldrich 99.9%). All the chemicals were used without further purification.

FTIR, NMR and elemental analysis

The ionic liquids in the current study were characterised using Fourier transform infrared (FTIR) spectroscopy. The spectra were recorded in a Shimadzu FTIR-8400S Fourier Transform Infrared Spectrometer (FTIR) in the mid region (4000–400 cm⁻¹) using the Attenuated Total Reflectance ((MIRacle ATR) measurement mode. A CHNS-932 (LECO instruments) elemental analyzer was used to determine the individual percentage of elements in these ILs. A Bruker Avance 300 spectrophotometer was used to determine the ¹H and ¹³C NMR spectra of the present ILs using deuterated water (D₂O) and CDCl₃ as solvents.^{14,28}

A coulometric Karl Fischer titrator, DL 39 (Mettler Toledo) with CombiCoulomat fritless Karl Fischer reagent $(Merck)^{14,28}$ was used to determine the water content of the synthesised ILs. The measurement for each IL was made in triplicate and the average values are reported. The instruments used for the measurements of the physical properties in the present study were calibrated using Millipore quality water with known density, viscosity and refractive index. The data established by our research group^{14,29,30} for the ILs 1-butyl-3-propanenitrile imidazolium bromide; [C₂CN Bim]Br, bis-(2-hydroxyethyl)ammonium acetate; BHEAA and 1-hexyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide; [C₆Mim]NTf₂ were used for the validation of the accuracy and reproducibility of the instruments.

Bromide measurements were conducted by ion chromatography (Metrohm Model 761 Compact IC) with a (150×4.0) mm analytical column (Metrosep A Supp 5-150) and a (5.0×4.0) mm guard column (Metrosep A Supp 4/5).²⁸ The samples were diluted by dissolving 0.5 cm⁻³ of each IL in 10 cm⁻³ of acetonitrile then the volume was made up to 50 cm⁻³ with deionised water. The analysis of the results was made using Metrodata IC Net 2.3 software.

1-Alkyl-3-propanenitrile imidazolium bromide [C₂CN C_nim]Br. A 250 mL, round-bottomed flask equipped with a heating oil bath, a nitrogen inlet adapter, magnetic stirrer and reflux condenser was flushed with dry nitrogen. The flask was charged with imidazole (0.5 mol, 34.04 g) in methanol and mixed with acrylonitrile (0.6 mol, 39.5 mL). The solution was heated under reflux and nitrogen atmosphere at 50-55 °C for 10 h and then cooled to room temperature. The volatile materials were removed from the mixture under reduced pressure at 70 °C. Nitrile-functionalised IL was synthesised by the direct quaternisation reaction of the imidazole-bearing nitrile group with 1-bromobutane.¹⁴ (0.5 mol, 53.9 mL) of 1-bromobutane was added and the mixture was stirred and maintained at 70 °C under a nitrogen atmosphere for 48 h. The resulting compound was cooled to room temperature and washed with ethyl acetate three times and the remaining solvent was removed at 80 °C under reduced pressure. It was then dried in a vacuum oven for 72 h¹⁴ to give 1-butyl-3propanenitrile imidazolium bromide [C₂CN Dim]Br.

A similar procedure was used to synthesise 1-decyl-3propanenitrile imidazolium bromide [C_2CN Dim]Br where (0.5 mol, 103.8 mL) of 1-bromodecane was used.

[C₂CN Bim]Br; ¹H NMR (CDCl₃): $\delta = 0.98$ (t, 3H, CH₂–*CH*₃), 1.38 (m, 2H, CH₂–*CH*₂–CH₃), 1.90 (m, 2H, N–CH₂–*CH*₂–CH₂–), 3.21 (t, 2H, N–*CH*₂–CH₂–CN), 4.29 (t, 2H, N–*CH*₂–*CH*₂–CN), 4.60 (t, 2H, N–*CH*₂–(CH₂)₂–CH₃), 4.75 (s, 1H, N–*CH*–*CH*), 7.79 (s, 1H, N–*CH*–CH), 9.24 (s, 1H, N–*CH*–N) ppm. ¹³C NMR (75 MHz; CDCl₃) = 136.80, 121.54, 120.58, 117.28, 48.22, 42.96, 30.02, 19.08, 17.99. 11.43 ppm. FTIR-ATR ν_{max}/cm^{-1} : 2246 and 1562 (CN), 2923 and 2854 (C–H).

Elemental analysis: found C, 46.62; H, 6.01; N, 16.97%. $C_{10}H_{16}N_3Br$ requires C, 46.52; H, 6.26; N, 16.28%.

[C₂CN Dim]Br; $\delta_{\rm H}$ (300 MHz; CDCl₃): = 0.47 (15 H, t, CH₃CH₂), 0.93 (12 H, br m, CH₂), 1.54 (2 H, t, CH₂CH₂N), 3.05 (2 H, t, CH₂CH₂CN), 3.92 (2 H, t, CNCH₂), 4.54 (2 H, t, NCH₂), 7.27(1 H, s, CHN), 7.88(1 H, s, CHN), 9.82 (1 H, s, NCHN) ppm. ¹³C NMR (75 MHz; CDCl₃) = 137.02, 122.95, 121.13, 116.87, 49.61, 45./9, 31.23, 29.68, 28.21, 23.12, 22.65, 18.97, 13.42 ppm. FTIR-ATR $\nu_{\rm max}/{\rm cm}^{-1}$: 2244 and 1562 (CN), 2921 and 2852 (C–H).

Elemental analysis: found C, 56.22; H, 8.04; N, 12.59%. $C_{16}H_{28}N_3Br$ requires C, 56.13; H, 8.26; N, 12.28%.

1-Alkyl-3-propanenitrile imidazolium dioctylsulfosuccinate $[C_2CN C_n im]DOSS$. $[C_2CN Bim]Br$ (0.03 mol) and sodium dioctylsulfosuccinate (0.03 mol) in acetone was mixed together in a 250 mL round-bottomed flask. The mixture was stirred at room temperature for 48 h. The solid precipitate formed was separated and the solvent removed *in vacuo*. The resulting pale yellow viscous compound was cooled to room temperature and washed with ethyl acetate and diethyl ether. It was then

dried in a vacuum oven for 48 h to give 1-butyl-3-propanenitrile imidazolium dioctylsulfosuccinate [C₂CN Dim]DOSS. A similar procedure was repeated to synthesise 1-decyl-3-propanenitrile imidazolium dioctylsulfosuccinate [C₂CN Dim]DOSS by replacing [C₂CN Bim]Br with [C₂CN Dim]Br.

[C₂CN Bim]DOSS; $\delta_{\rm H}$ (300 MHz; CDCl₃): = 0.84 (15 H, t, *CH*₃CH₂), 1.24 (16 H, br m, *CH*₂), 1.38 (4 H, d, O*CH*₂CH), 1.62 (2 H, t, *CH*₂CH₂N), 1.91 (2 H, d, CO*CH*₂CH), 3.19 (2 H, t, *CH*₂CH₂CN), 3.98 (2 H, t, *CNCH*₂), 4.05 (4 H, d, O*CH*₂CH), 4.28 (2 H, t, *NCH*₂), 4.71 (1 H, t, *CH*SO₃), 7.34 (1 H, s, *CHN*), 7.80 (1 H, s, *CHN*), 9.95 (1 H, s, *NCHN*) ppm. ¹³C NMR (75 MHz; CDCl₃) = 171.26, 168.56, 136.68, 122.64, 116.67, 67.53, 66.92, 62.06, 48.21, 48.00, 47.78, 47.57, 47.36, 30.21, 28.81, 22.75, 19.15, 13.24, 13.20 ppm. FTIR-ATR $\nu_{\rm max}/{\rm cm}^{-1}$: 2248 and 1564 (CN), 2929 and 2871 (C–H), 1213 and 1035 (SO₃), 1730 (C=O), 1161 (C–O–C).

Elemental analysis: found C, 59.89, H, 9.15; N, 6.90; S, 5.41%. $C_{30}H_{54}N_3O_7S$ requires C, 59.97; H, 9.06; N, 6.99; S, 5.34%.

[C₂CN Dim]DOSS; $\delta_{\rm H}$ (300 MHz; CDCl₃): = 0.88 (15 H, t, *CH*₃CH₂), 1.32 (28 H, br m, *CH*₂), 1.55 (4 H, d, O*CH*₂CH), 1.87 (2 H, t, *CH*₂CH₂N), 2.83 (2 H, d, CO*CH*₂CH), 3.21 (2 H, t, *CH*₂CH₂CN), 3.96 (2 H, t, CN*CH*₂), 4.17 (4 H, d, O*CH*₂CH), 4.24 (2 H, t, N*CH*₂), 4.72 (1 H, t, *CH*SO₃), 7.34 (1 H, s, *CH*N), 7.88(1 H, s, *CH*N), 9.62 (1 H, s, N*CH*N) ppm. ¹³C NMR (75 MHz; CDCl₃) = 171.40, 169.37, 137.32, 123.31, 121.93, 117.05, 68.01, 50.23, 45.32, 38.58, 31.82, 30.03, 29.22, 28.84, 26.26, 23.39, 22.90, 19.67, 13.99, 10.83 ppm. FTIR-ATR $\nu_{\rm max}/{\rm cm}^{-1}$: 2250 and 1564 (CN), 2925 and 2873 (C–H), 1223 and 1037 (SO₃), 1731 (C=O), 1159 (C–O–C).

Elemental analysis: found C, 63.03; H, 9.65; N, 6.04; S, 4.73%. $C_{36}H_{66}N_3O_7S$ requires C, 63.12; H, 9.71; N, 6.13; S, 4.68%.

1-Alkyl-3-propanenitrile imidazolium dodecylsulfate [C₂CN Cnim]DDS. [C₂CN Bim]Br (0.04 mol) and sodium dodecylsulfate $C_{12}H_{25}OSO_3Na$ (0.04 mol) were mixed in 40 mL of hot deionized water (60 °C). The mixture was stirred at room temperature for 48 h. The water was slowly removed under vacuum at 80 °C then 50 mL of CH₂Cl₂ was added to the precipitate and the mixture was filtrated. The viscous extract was then washed with deionized water and the washing was repeated until it was bromide-free. The remaining solvent was removed at 80 °C under vacuum and then dried in a vacuum oven for 48 h to afford the viscous gel product, 1-butyl-3propanenitrile imidazolium dodecylsulfate [C₂CN Bim]DDS. A similar procedure was repeated to synthesise 1-decyl-3propanenitrile imidazolium dodecylsulfate [C₂CN Dim] by replacing [C₂CN Bim]Br with [C₂CN Dim]Br.

[C₂CN Bim]DDS; $\delta_{\rm H}$ (300 MHz; D₂O): = 1.01 (6 H, t, *CH*₃CH₂), 1.45 (20 H, br m, *CH*₂), 1.98 (2 H, t, *CH*₂CH₂O), 3.30 (2 H, t, *CH*₂CH₂N), 3.33 (2 H, t, *CH*₂CH₂CN), 4.39 (2 H, t, *CNCH*₂), 4.70 (2 H, t, *OCH*₂CH₂), 4.79 (2 H, t, *NCH*₂CH₂), 7.75 (2 H, s, *CH*N), 7.81 (1 H, s, *NCH*N) ppm. ¹³C NMR (75 MHz; D₂O) = 136.29, 123.32, 122.79, 118.04, 68.45, 49.8386, 45.12, 43.64, 32.23, 31.68, 30.13, 26.16, 22.87, 19.96, 19.59, 19.20, 14.05, 13.25 ppm.

FTIR-ATR $\nu_{\text{max}}/\text{cm}^{-1}$: 2252 and 1564 (CN), 2923 and 2865 (C–H), 1215 and 1163 (SO₃).

Elemental analysis: found C, 59.35, H, 9.61; N, 9.49; S, 7.15%. $C_{22}H_{42}N_3O_4S$ requires C, 59.43; H, 9.52; N, 9.49; S, 7.15%.

[C₂CN Dim]DDS; $\delta_{\rm H}$ (300 MHz; D₂O): = 0.88 (6 H, t, CH_3 CH₂), 1.29 (20 H, br m, CH_2), 1.36 (12 H, br m, CH_2), 1.90 (2 H, t, CH_2 CH₂O), 3.17 (2 H, t, CH_2 CH₂N), 3.20 (2 H, t, CH_2 CH₂CN), 3.98 (2 H, t, $CNCH_2$), 4.25 (2 H, t, OCH_2 CH₂), 4.58 (2 H, t, NCH_2 CH₂), 7.75 (2 H, s, CHN), 7.77 (1 H, s, NCHN) ppm. ¹³C NMR (75 MHz; D₂O) = 122.96, 122.53, 116.5245, 109.39, 67.84, 48.37, 47.7243, 45.07, 31.74, 29.49, 29.45, 29.23, 28.19, 25.94, 25.66, 22.43, 18.62, 13.17 ppm. FTIR-ATR $\nu_{\rm max}/{\rm cm}^{-1}$: 2250 and 1564 (CN), 2921 and 2872 (C–H), 1218 and 1163 (SO₃).

Elemental analysis: found C, 63.68; H, 10.37; N, 7.98; S, 6.01%. $C_{28}H_{54}N_3O_4S$ requires C, 63.60; H, 10.29; N, 7.95; S, 6.06%.

1-Butyl-3-propanenitrile imidazolium benzenesulfonate [C₂CN Bim]BS. 1-butyl-3-propanenitrile imidazolium benzenesulfonate [C₂CN Bim]BS was synthesised by following the same procedure as that described for [C₂CN Bim]DDS by adding sodium benzenesulfonate C₆H₅SO₃Na (0.04 mol, 7.21 g) to (0.04 mol, 10.33 g) [C₂CN Bim]Br.

[C₂CN Bim]BS; $\delta_{\rm H}$ (300 MHz; D₂O): = 0.83 (3 H, t, *CH*₃CH₂), 1.28 (2H, t, *CH*₂CH₃), 1.87 (2 H, t, *CH*₂CH₂N), 3.17 (2 H, t, *CH*₂CH₂CN), 4.23 (2 H, t, *CNCH*₂CH₂), 4.57 (2 H, t, *NCH*₂CH₂), 7.54 (3 H, d,*CH*CHCH), 7.58 (1 H, s, *CHN*), 7.63 (1 H, s, *CHN*), 7.78 (1 H, s, *NCHN*), 8.98 (2 H, br d, CHCSO₃) ppm. ¹³C NMR (75 MHz; D₂O) = 135.82, 131.53, 129.04, 125.41, 123.12, 117.93, 50.00, 44.84, 30.38, 29.10, 25.01, 21.82, 19.36, 13.32 ppm. FTIR-ATR $\nu_{\rm max}/{\rm cm}^{-1}$: 2248 and 1562 (CN), 2960 and 2871 (C–H), 1190 and 1031 (SO₃).

Elemental analysis: found C, 57.22, H, 6.54; N, 12.57; S, 9.48%. $C_{16}H_{22}N_3O_3S$ requires C, 57.12; H, 6.59; N, 12.49; S, 9.53%.

1-Butyl-3-propanenitrile imidazolium trifluoromethanesulfonate [C₂CN Oim]TFMS. 1-butyl-3-propanenitrile imidazolium trifluoromethanesulfonate [C₂CN Oim]TFMS was synthesised by following the same procedure by adding sodium trifluoromethanesulfonate CF₃SO₃Na (0.04 mol, 6.88 g) to (0.04 mol, 10.33 g) [C₂CN Bim]Br.

[C₂CN Bim]TFMS; $\delta_{\rm H}$ (300 MHz; D₂O): = 0.90 (3 H, t, *CH*₃CH₂), 1.29 (2 H, t, *CH*₂CH₃), 1.852 (H, t, *CH*₂CH₂N), 3.15 (2 H, t, *CH*₂CH₂CN), 4.23 (2 H, t, *CNCH*₂CH₂), 4.56 (2 H, t, *NCH*₂CH₂), 7.54 (1 H, s, *CHN*), 7.61 (1 H, s, *CHN*), 8.94 (1 H, s, *NCHN*) ppm. ¹³C NMR (75 MHz; D₂O) = 135.73, 123.04, 122.33, 121.34, 117.92, 49.71, 44.80, 31.17, 19.24, 18.77, 12.66 ppm. FTIR-ATR $\nu_{\rm max}/{\rm cm}^{-1}$: 2254 and 1564 (CN), 2964 and 2875 (C–H), 1249 and 1029 (SO₃), 1226 and 1159 (CF₃).

Elemental analysis: found C, 40.29, H, 4.94; N, 12.79; S, 9.73%. C₁₁H₁₆F₃N₃O₃S requires C, 40.36; H, 4.93; N, 12.84; S, 9.80%.

Density and viscosity measurements

The density and viscosity of all ionic liquids was measured at 298.15 K at atmospheric pressure using a Stabinger viscometer (Anton–Paar model SVM3000). The temperature was

Refractive index measurements

An ATAGO programmable digital refractometer (RX-5000 alpha) with a measuring accuracy of $\pm 4 \times 10^{-5}$ was used to measure the refractive index of various ILs at 298.15 K. The temperature of the apparatus was controlled to within ± 0.05 °C. The apparatus was calibrated and checked before each series of measurements using pure organic solvents with known refractive indices.^{14,28–30} Dried samples kept in desiccators were directly placed into the measuring cell. Reproducibility of the results was confirmed by performing three experiments for each IL in the temperature studied in the present work.

Thermogravimetry measurements

A PerkinElmer, Pyris V-3.81 was used to measure the decomposition temperatures of the synthesised ILs. The samples were placed in aluminium pans under a nitrogen atmosphere at a heating rate of 5 °C min⁻¹. The measured start temperature (T_s) and decomposition temperature (T_d) are presented in Table 1.

The melting, crystallisation, and glass transition temperatures were measured by differential scanning calorimetry using a 5 °C min⁻¹ heating rate. A Mettler-Toledo differential scanning calorimeter (DSC822e) with Mettler-Toledo STAR^e software was used for the measurements.

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References

- P. Husson-Borg, V. Majer and M. F. Costa Gomes, J. Chem. Eng. Data, 2003, 48, 480–485.
- 2 J. N. C. Lopes, T. C. Cordeiro, J. M. S. S. Esperancüa, H. J. R. Guedes, S. Huq, L. P. N. Rebelo and K. R. Seddon, *J. Phys. Chem. B*, 2005, **109**, 3519–3525.
- 3 M. G. Freire, P. J. Carvalho, A. M. Fernandes, I. M. Marrucho, A. J. Queimada and J. A. P. Coutinho, J. Colloid Interface Sci., 2007, **314**, 621–630.
- 4 C. Chiappe and D. Pieraccini, J. Org. Chem., 2004, 69, 6059-6064.

- 5 M. Tariq, P. A. S. Forte, M. F. Costa, J. N. Canongia and L. P. N. Rebelo, J. Chem. Thermodyn., 2009, 41, 790–798.
- 6 J. Vila, P. Ginés, J. M. Pico, O. C. Franj, E. Jiménez, L. M. Varela and O. Cabeza, *Fluid Phase Equilib.*, 2006, 242, 141–146.
- 7 C. Ye and J. n. M. Shreeve, J. Phys. Chem. B, 2007, 111, 1456–1461.
- 8 Y. Zhong, H. Wang and K. Diao, J. Chem. Thermodyn., 2007, 39, 291–296.
- 9 Z. Fei, D. Zhao, D. Pieraccini, W. H. Ang, T. J. Geldbach, R. Scopelliti, C. Chiappe and P. J. Dyson, *Organometallics*, 2007, 26, 1588–1598.
- 10 F. Mazille, Z. Fei, D. Kuang, D. Zhao, S. M. Zakeeruddin, M. Grätzel and P. J. Dyson, *Inorg. Chem.*, 2006, **45**, 1585–1590.
- 11 J. Y. Kim, T. H. Kim, D. Y. Kim, N.-G. Park and K.-D. Ahn, J. Power Sources, 2008, 175, 692–697.
- 12 Q. Zhang, Z. Li, J. Zhang, S. Zhang, L. Zhu, J. Yang, X. Zhang and Y. Deng, J. Phys. Chem. B, 2007, 111, 2864–2872.
- 13 A. E. Visser, R. P. Swatloski, W. M. Reichert, R. Mayton, S. Sheff, A. Wierzbicki, J. H. Davis and R. D. Rogers, *Environ. Sci. Technol.*, 2002, 36, 2523–2529.
- 14 A. K. Ziyada, C. D. Wilfred, M. A. Bustam, Z. Man and T. Murugesan, J. Chem. Eng. Data, 2010, 55, 3886–3890.
- 15 D. Zhao, Z. Fei, R. Scopelliti and P. J. Dyson, *Inorg. Chem.*, 2004, 43, 2197–2205.
- 16 P. Nockeman, M. Pellens, K. V. Hecke, L. V. Meervelt, J. Wouters, B. Thijs, E. Vanecht, T. N. Parac-Vogt, H. Mehdi, S. Schaltin, J. Fransaer, S. Zahn, B. Kirchner and K. Binnemans, *Chem.-Eur. J.*, 2010, **16**, 1849–1858.
- 17 M. Yao, M. Fan, Y. Liang, F. Zhou and Y. Xia, Wear, 2010, 268, 67–71.
- 18 G. Yua, S. Yana, F. Zhoub, X. Liub, W. Liub and Y. Liang, *Tribol. Lett.*, 2007, 25, 197–205.
- 19 A. B. Pereiro, F. Santamarta, E. Tojo, A. Rodríguez and J. Tojo, J. Chem. Eng. Data, 2006, 51, 952–954.
- 20 D. W. Fang, W. Guan, J. Tong, Z. W. Wang and J. Z. Yang, J. Phys. Chem. B, 2008, 112, 7499–7505.
- 21 L. Glasser and H. D. B. Jenkins, *Thermochim. Acta*, 2004, **414**, 125–130.
- 22 J.-Z. Yang, Q.-G. Zhang, B. Wang and J. Tong, J. Phys. Chem. B, 2006, 110, 22521–22524.
- 23 L. Glasser, Thermochim. Acta, 2004, 421, 87-93.
- 24 J. Crosthwaite, M. Muldoon, J. Dixon, J. Anderson and J. Brennecke, J. Chem. Thermodyn., 2005, 37, 559–568.
- 25 K. Lava, K. Binnemans and T. Cardinaels, J. Phys. Chem. B, 2009, 113, 9506–9511.
- 26 C. M. Gordon, J. D. Holbrey, A. R. Kennedy and K. R. Seddon, J. Mater. Chem., 1998, 8, 2627–2636.
- 27 J. Holbrey and K. Seddon, J. Chem. Soc., Dalton Trans., 1999, 2133–2140.
- 28 N. M. Yunus, M. I. A. Mutalib, Z. Man, M. A. Bustam and T. Murugesan, J. Chem. Thermodyn., 2010, 42, 491–495.
- 29 K. A. Kurnia, C. D. Wilfred and T. Murugesan, J. Chem. Thermodyn., 2009, 41, 517–521.
- 30 A. Muhammad, M. I. A. Mutalib, C. D. Wilfred, T. Murugesan and A. Shafeeq, J. Chem. Thermodyn., 2008, 40, 1433–1438.
- 31 A. E. Visser, R. P. Swatloski, W. M. Reichert, R. Mayton, S. Sheff, A. Wierzbicki, J. H. Davis Jr and R. D. Rogers, *Environ. Sci. Technol.*, 2002, 36, 2523–2529.