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Thermophysical properties of imidazolium tricyanomethanide ionic liquids: experiments and molecular simulation†

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The low-viscous tricyanomethanide ([TCM][−])-based ionic liquids (ILs) are gaining increasing interest as attractive fluids for a variety of industrial applications. The thermophysical properties (density, viscosity, surface tension, electrical conductivity and self-diffusion coefficient) of the 1-alkyl-3-methylimidazolium tricyanomethanide [C_nmim][TCM] (*n* = 2, 4 and 6–8) IL series were experimentally measured over the temperature range from 288 to 363 K. Moreover, a classical force field optimized for the imidazolium-based [TCM][−] ILs was used to calculate their thermodynamic, structural and transport properties (density, surface tension, self-diffusion coefficients, viscosity) in the temperature range from 300 to 366 K. The predictions were directly compared against the experimental measurements. The effects of anion and alkyl chain length on the structure and thermophysical properties have been evaluated. In cyano-based ILs, the density decreases with increasing molar mass, in contrast to the behavior of the fluorinated anions, being in agreement with the literature. The contribution per −CH₂− group to the increase of the viscosity presents the following sequence: [PF₆][−] > [BF₄][−] > [Tf₂N][−] > [DCA][−] > [TCB][−] > [TCM][−]. [TCM][−]-based ILs show lower viscosity than dicyanamide ([DCA][−])- and tetracyanoborate ([TCB][−])-based ILs, while the latter two exhibit a crossover which depends both on temperature and the alkyl chain length of the cation. The surface tension of the investigated ILs decreases with increasing alkyl chain length. [C₂mim][TCM] shows an outlier behavior compared to other members of the homologous series. The surface enthalpies and surface entropies for all the studied systems have been calculated based on the experimentally determined surface tensions. The relationship between molar conductivity and viscosity was analyzed using the Walden rule. The experimentally determined self-diffusion coefficients of the cations are in good agreement with the molecular simulation predictions, in which a decrease of the self-diffusion of the cations with increasing alkyl chain length is observed with a simultaneous increase in viscosity and for the longer alkyl lengths the anion becomes more mobile than the cation.

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1 Introduction

Ionic liquids (ILs) are salts composed of an organic cation and an organic/inorganic anion, exhibiting melting temperatures below 100 °C. The possible tuning of the thermophysical properties by varying the nature of the ions and the length and nature of the (alkyl) chains attached to them is one of the many advantages of ILs, which contributes to the design of “greener” systems for specific applications. As a result, ILs have been investigated in several applications such as separation processes,^{1–4} synthesis,⁵ catalysis^{6,7} and electrochemistry.⁸

The possibility of systematically adjusting the thermophysical properties is one of the main advantages of IL systems. Therefore, the knowledge and understanding of structure–property relationships of ILs is indispensable.^{9–11} Large efforts have been made in order to determine these properties experimentally or

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by theoretical/molecular simulation methods^{12–20} and several predictive models have been proposed.^{11,21–24}

Currently it is well accepted that ILs are highly structured fluids in which the ion pairs arrange themselves into polar and non-polar domains.^{25–30} The structural segregation in these systems depends on the relative size of the high-charge and low-charge regions in each ion and the size of the alkyl chain length.^{25–34} The effect of the structural segregation on the thermophysical properties has been reported in literature for the extended series of ILs $[C_nC_1im][Tf_2N]$ ($n = 2–8, 10$, and 12), $[C_nC_nim][Tf_2N]$ ($n = 2–12$) and $[C_nC_1im][PF_6]$ ($n = 4–8$).^{35–41} In the rest of the paper, C_1 will be denoted as “m”, for methyl. ILs with fluorine-based anions have been widely explored in the literature, mainly due to their high thermal stability and not so high viscosity, and less attention has been given to non-fluorine based ILs. Cyano-based ILs have a significantly lower viscosity than fluorine-based ILs, making them more attractive for industrial applications.⁴² These systems have been used in several studies focused on dye-sensitized solar cells,^{43,44} liquid–liquid and vapor–liquid separation^{45–48} and CO_2 solubility.^{2,49–51} Computational studies on cyano-based ILs are scarce. $[C_2mim][TCM]$ was the only $[TCM]^-$ -based IL investigated by Borodin⁵² using a complex polarizable force field. Recently, a classical force field has been optimized and validated for $[C_nmim][TCM]$ ($n = 2, 4, 6$, and 8) IL family.⁵³ The calculated transport properties were found to be in very good agreement with the experiments.⁵³ Also, very lately $[C_2mim][TCM]$ and its mixtures with water were simulated.⁵⁴

Imidazolium based ILs containing the anion tricyanomethanide ($[C(CN)_3]^-$ or $[TCM]^-$) are low-viscous ILs,⁵⁵ which have been currently successfully evaluated concerning their potential use in gas separation processes.^{2,49,50} Some thermophysical properties for imidazolium $[TCM]^-$ -based ILs have been recently reported in the literature.^{56,57} Neves *et al.*⁵⁸ performed for the first time a consistent and comprehensive structure–property study for a set of imidazolium-based ILs with cyano-functionalized anions, where the effect of the anion on the studied properties was investigated. However, the effect of the chemical nature of those ILs and their impact on the structural segregation of ILs is not clear.

In the present work, the thermophysical properties of 1-alkyl-3-methylimidazolium tricyanomethanide ILs, $[C_nmim][TCM]$ (with $n = 2, 4$ and $6–8$), specifically density, viscosity, surface tension and electrical conductivity, as well as their dependency on temperature were measured. Additionally, the self-diffusion coefficients of the cations have also been determined experimentally at 298.15 K and for $[C_2mim][TCM]$ from 293 to 323 K. The influence of the alkyl chain length of the cation on the thermophysical properties is discussed and compared to studies available in literature. The effect of the $[TCM]^-$ anion on the structure of the bulk liquid and on the thermophysical properties of systems studied is further explored with the aid of molecular simulation. The microscopic characteristics and the macroscopic behavior of the systems under study are examined. Thermodynamic, structural, surface and transport properties are calculated in the temperature range between 300 and 366 K and

the predictions are directly compared with the results of experimental measurements.

2 Experimental details

2.1 Materials and purification

The studied, $[C_nmim][TCM]$ ($n = 2, 4$ and $6–8$) ILs were provided by Ionic Liquids Technologies GmbH (IoLiTec) with the stated purity better than 98%. All the ILs were dried under vacuum (< 10 Pa), for at least 48 h, at moderate temperature (323 K) and constant stirring. The water content was determined using a Metrohm 795 KFT Karl Fischer titrator. For all the ILs, the water content after drying was below 200 ppm. No further purification was performed. Details of the ILs examined are provided in Table 1.

2.2 Densities and viscosities

The density, ρ , and the viscosity, η , measurements were performed at atmospheric pressure and in the temperature range of 288.15 to 363.15 K, using an automated SVM 3000 Anton Paar Stabinger viscometer. For each IL, at least three independent measurements were performed using the same experimental conditions and different samples. The apparatus was calibrated by measuring the density and viscosity of three certified reference standard calibration samples, APN7.5, APN26 and APN415 (certified references, ISO 17025/ISO guide 34). The reproducibility of the dynamic viscosity and density measurements is according to the manufacturer 0.35% and 0.5 kg m^{-3} , respectively. From 288.15 to 378.15 K the uncertainty of temperature is within 0.02 K.

2.3 Surface tension

The surface tension, γ , was measured at atmospheric pressure in the temperature range between 298.15 and 341.15 K with a Krüss K11 MK4 tensiometer using the plate method. The roughened platinum plate's dimensions delivered by Krüss are $19.9 \times 0.2 \times 10 \text{ mm}$ ($W \times D \times H$). The measuring range is between 1 and 999 mN m^{-1} , the resolution is 0.1 mN m^{-1} , the standard deviation is 0.03 mN m^{-1} and the temperature control ranges from 263.15 to 403.15 K. In the plate method, the thermostated cell containing the sample is raised until contact with the surface is registered. The tensile force acting on the plate when in contact with the interface is recorded and used to calculate the surface tension using the Wilhelmy equation, which is implemented within the tensiometer software. The reported

Table 1 Specifications of the ILs used in this work

IL	Source	Purity ^a	$M/\text{g mol}^{-1}$
$[C_2mim][TCM]$	IoLiTec	> 0.98	201.23
$[C_4mim][TCM]$	IoLiTec	> 0.99	229.28
$[C_6mim][TCM]$	IoLiTec	> 0.98	257.33
$[C_7mim][TCM]$	IoLiTec	> 0.98	271.37
$[C_8mim][TCM]$	IoLiTec	> 0.98	285.39

^a Purity (mole fraction) was provided by the supplier.

value is an average of at least three subsequent measurements with a standard deviation of $<0.1 \text{ mN m}^{-1}$.

2.4 Electrical conductivity

Electrical conductivity measurements were performed using a Jenway 4020 conductivity meter within a temperature range between 293.15 and 369.15 K. Jenway 4020 is a microprocessor controlled instrument with measuring range from 0.01 to 1000 $\mu\text{S cm}^{-1}$. The equipment was calibrated with a KCl solution, with an accuracy of 0.5%. The operating temperature range of the equipment is 273.15 to 383.15 K. The temperature measurement is accurate within 0.1 K.

2.5 Self-diffusion coefficients

The self-diffusion coefficients, D_{self} , of the imidazolium cations $[\text{C}_2\text{mim}]^+$, $[\text{C}_4\text{mim}]^+$, $[\text{C}_6\text{mim}]^+$ and $[\text{C}_8\text{mim}]^+$ were derived from the pulse-field gradient spin-echo NMR measurements using ^1H nuclei in the methyl, ethyl, butyl, hexyl and octyl chains of the cation. A bipolar pulse longitudinal eddy current delay was applied as pulse sequence with a sine gradient shape. The temperature stability during the experiments was better than 0.5 K, and the absolute uncertainty in the temperature measurement was 0.05 K. The expanded uncertainty ($k = 2$) of the NMR experimental data was estimated to be less than 10%. A more detailed description of the methodology used is given elsewhere.^{59,60}

3 Molecular simulations

Molecular dynamics (MD) simulations of $[\text{C}_n\text{mim}][\text{TCM}]$ ($n = 2, 4, 6$ and 8) ILs were performed using the NAMD software code.⁶¹ An all-atom force field was used for the representation of the intra- and intermolecular interactions which has been optimized and validated for the $[\text{C}_n\text{mim}][\text{TCM}]$ IL family.⁵³ The systems consisted of 200 ion pairs and the initial structures were generated in MAPS (Materials and Processes Simulations platform, version 3.4.2, Scienomics SARL, Paris, France, 2004–2016) platform of Scienomics using a modified configuration bias Monte Carlo scheme.^{62,63} For each data point, atomic overlaps were eliminated by applying a conjugate gradient energy minimization method of 10^5 steps, followed by a short simulation of 5 ns in the canonical ensemble (NVT). A 25 ns simulation in the isobaric–isothermal ensemble (NPT) was then conducted and afterwards simulations of 20 ns were performed in the canonical ensemble (NVT) at the mean density, as obtained from the NPT simulations. Finally, simulation runs of the order of 30 ns were conducted in the microcanonical ensemble (NVE) to calculate the transport properties.

A Langevin piston with a 5 ps^{-1} damping factor was used to control the temperature and the Nosé–Hoover barostat was used for pressure control with an oscillation period equal to 200 fs and a damping factor of 100 fs. Particle-mesh Ewald method was used for the electrostatic interactions. Electrostatic interactions between atoms separated by three bonds were scaled by a factor of 0.5. A multiple time step was employed to speed up the MD simulations using the reversible reference

system propagator algorithm (rRESPA).^{64,65} For the NVT and NPT simulations, the reference time step was 1 fs and for the NVE ensemble 0.5 fs. Short-range non-bonded van der Waals interactions were calculated every 2 fs and the full electrostatic interactions were computed every 4 fs in the NVT and NPT runs and in case of NVE simulations these were calculated every 1 fs and 2 fs, respectively. A cutoff distance of 12 Å was used to truncate the van der Waals interactions using a switching function beyond 10.5 Å. A long-range correction was applied to the system's energy and virial to account for the neglected van der Waals forces due to switching and cutoff of the Lennard-Jones potential. The Lorentz–Berthelot mixing rules were used to calculate the force field parameters between unlike atoms.

3.1 Density and structure

The density was calculated during a simulation in the NPT ensemble. The structural characteristics of the systems under study were quantified by calculating the radial distribution functions (RDFs) between the centers of mass of the ions and between various atoms of the ions.

3.2 Transport properties

Calculation of the ion self-diffusion coefficients was performed using the Einstein relationship:

$$D = \frac{1}{6} \lim_{t \rightarrow \infty} \frac{d}{dt} \langle |\vec{r}_i(t) - \vec{r}_i(0)|^2 \rangle \quad (1)$$

where $\vec{r}_i(t)$ is the position of the i -th ion's center of mass at time t and the brackets denote the mean-square displacement (MSD) over all ion centers of mass. The diffusion coefficients were calculated in the Fickian regime, which is identified by a slope equal to unity in the $\log(\text{MSD})$ versus $\log(t)$ plot.

The shear viscosity was calculated using the following Green–Kubo relation:

$$\eta = \frac{V}{k_B T} \int_0^\infty \langle P_{ij}(t) P_{ij}(0) \rangle dt \quad (2)$$

where $P_{ij}(t)$ is the ij -element of the pressure tensor at time t ($i \neq j$).

3.3 Surface tension

In principle, the surface tension of an interface vertical to the z -dimension can be computed from the expression:⁶⁶

$$\gamma = \int_{-\infty}^{+\infty} (p_\perp(z) - p_\parallel(z)) dz \quad (3)$$

where $p_\perp$ and $p_\parallel$ are the components of the equilibrium pressure that are normal and perpendicular to the interface with $p_\perp = p_z$ and $p_\parallel = 0.5(p_x + p_y)$. In our case, the IL film defines two interfaces between the liquid and the vapor phase. Since these phases are in equilibrium, eqn (3) can be simplified further to express the surface as an ensemble average of the difference between the normal and the tangential components of the pressure:^{66,67}

$$\gamma = \frac{L_z}{2} \langle p_\perp - p_\parallel \rangle = \frac{L_z}{2} \left[\langle p_z \rangle - \frac{\langle p_x \rangle + \langle p_y \rangle}{2} \right] \quad (4)$$

The factor $\frac{1}{2}$ accounts for the presence of two interfaces defined by the film. The initial configurations for the surface tension simulations were obtained from the conducted NVE simulations of the bulk IL systems. In every case, two free surfaces were created by expanding the simulation box length corresponding to the z -dimension (L_z) by the same amount in each direction resulting in $3L_z$ box length along z -dimension. In this way a thin IL film parallel to the xy -plane is created.

Surface tension was calculated in the NVT ensemble using the simulation setup-described for the NVE simulations. Only in this case a mesh-based long-range dispersion correction was applied for the non-bonded interactions (both Lennard Jones and electrostatic).^{68,69} For each system of interest, the initial configuration was subjected to a 5 ns equilibration run in order to relax the IL film. Subsequently prolonged production simulations of duration varying from 30–40 ns were performed. The LAMMPS molecular simulation package⁷⁰ was used for the surface tension calculations.

4 Results and discussion

4.1 Density

The experimental data for the density of $[C_n\text{mim}][\text{TCM}]$ are available in Table S1 of the (ESI[†]). A graphical representation of the densities against the temperature is depicted in Fig. 1 and the deviations compared to the available literature data are shown in Fig. S1 (ESI[†]). The densities calculated *via* molecular simulations are also represented in Fig. 1. The deviation of calculations from the experimental data is below 1.5% verifying the ability of the force field to accurately reproduce the density for the whole $[C_n\text{mim}][\text{TCM}]$ IL family. The experimentally determined densities presented in this work are in excellent agreement with the literature data, with deviations below 0.15%.^{56,58,71–75} In Fig. S1 (ESI[†]), these deviations are presented

as a function of temperature. Only for $[C_2\text{mim}][\text{TCM}]$ larger relative deviations were observed (2.3%⁷⁶ and –0.7%,⁷⁷ respectively), which could be related to the purity and water content of the samples. However, in both studies^{76,77} no information about purity, water content and associated uncertainty of the density was described. To the best of our knowledge, no literature data for $[C_7\text{mim}][\text{TCM}]$ are available.

The experimental density data, in the studied temperature range, can be represented by a second order polynomial equation:

$$\rho(T) = a + bT + cT^2 \quad (5)$$

where T is temperature in K and a , b , and c are the fitting parameters listed in Table S2 (ESI[†]), together with the molar volumes ($V_m = M/\rho$) at 298.15 K. The volumetric changes with temperature can also be extracted from the density data (as described by eqn (5)) to obtain the isobaric thermal expansion.

As expected, the densities of the $[\text{TCM}]^-$ -based ILs decrease with increasing temperature. Additionally, a decrease of the densities with increasing alkyl chain length of the imidazolium cation is observed. This is in agreement with the previous reported work in literature on imidazolium-based ILs.^{11,58,60,78–80} The gradual linear increase of V_m for the $[\text{TCM}]^-$ -based ILs of $(16.53 \pm 0.02) \text{ cm}^3 \text{ mol}^{-1}$ per methylene group, $-\text{CH}_2-$, is in agreement with other imidazolium-based ILs reported in the literature^{56,59,60,78,79,81} and with the medium-chain n -alkanes $[(16.21 \pm 0.05) \text{ cm}^3 \text{ mol}^{-1}; C_n\text{H}_{2n+2}, n = 9\text{--}16]$.^{82,83} This tendency is independent of the anion paired with the imidazolium cation and is for instance also applicable for alkylsulfonate and alkyl-sulfate anions.⁸⁴

With the aim of evaluating the effect of the anion on the densities of $[C_n\text{mim}]^+$ based ILs, the densities at $T = 298.15 \text{ K}$ as a function of the number of carbons of the alkyl chain, $n(\text{C})$, are depicted in Fig. 2. The fluorine-based ILs have higher densities (denser packing) than those containing cyano-anions due to the contribution of the heterogeneous and heavy atoms. In addition, the shape/symmetry and high charge distribution of fluorine-based ILs enhances a more selective distribution around the charged cation. This can be related with a higher structural organization in the bulk liquid.^{85,86} A higher dependency of the densities on the alkyl chain length of the cation is observed for the ILs with fluorine-based anions. As the alkyl chain increases, the higher organization of the fluorinated ILs is more affected leading to a higher contribution of the methylene group, $-\text{CH}_2-$, to the density decrease. This can be related with the stronger ion pairing of the fluorinated ILs as a result of their higher dispersive interactions.⁸⁵

The anion effect on the densities was further explored considering a common cation, 1-butyl-3-methylimidazolium cation ($[C_4\text{mim}]^+$). The representation of the densities at 298.15 K against the molar mass of the anion is shown in Fig. 3. For this analysis the densities of $[C_4\text{mim}][\text{FAP}]$,⁸⁷ $[C_4\text{mim}][\text{Tf}_2\text{N}]$,⁷⁹ $[C_4\text{mim}][\text{PF}_6]$,⁷⁸ $[C_4\text{mim}][\text{BF}_4]$,⁸¹ $[C_4\text{mim}][\text{SCN}]$,⁵⁸ $[C_4\text{mim}][\text{DCA}]$ ^{58,88} and $[C_4\text{mim}][\text{TCB}]$,⁵⁶ were also considered.

The influence of the anion on the densities has been explored previously by Kolbeck *et al.*⁹⁰ and later by Neves *et al.*⁵⁸ In both

Fig. 1 Density as a function of temperature for the $[C_n\text{mim}][\text{TCM}]$ IL series. Experimental data: $\blacktriangleleft$ – $[C_2\text{mim}][\text{TCM}]$; $\blacklozenge$ – $[C_4\text{mim}][\text{TCM}]$; $\bullet$ – $[C_6\text{mim}][\text{TCM}]$; $\blacksquare$ – $[C_7\text{mim}][\text{TCM}]$; $\blacktriangle$ – $[C_8\text{mim}][\text{TCM}]$; molecular simulation data: $\triangleleft$ – $[C_2\text{mim}][\text{TCM}]$; $\diamond$ – $[C_4\text{mim}][\text{TCM}]$; $\circ$ – $[C_6\text{mim}][\text{TCM}]$; $\triangle$ – $[C_8\text{mim}][\text{TCM}]$. The solid lines represent the second order polynomial fitting of the experimental data (eqn (5)).

Fig. 2 Densities, at $T = 298.15$ K and 0.1 MPa, as a function of the number of carbons of the alkyl chain, $n(C)$. This work: $\blacktriangle$ – $[C_n\text{mim}][\text{TCM}]$ ($n = 2, 4$ and $6-8$). Literature: $\bullet$ – $[C_n\text{mim}][\text{Tf}_2\text{N}]$ ($n = 2-10$);^{79,89} $\blacklozenge$ – $[C_n\text{mim}][\text{PF}_6]$ ($n = 4-9$);⁷⁸ $\blacktriangleleft$ – $[C_n\text{mim}][\text{BF}_4]$ ($n = 2, 4, 6$ and 8);⁸¹ $\bullet$ – $[C_n\text{mim}][\text{TCB}]$ ($n = 2, 4, 6, 8$ and 10);^{56,59,60} $\bullet$ – $[C_n\text{mim}][\text{DCA}]$ ($n = 2, 4$ and 6).^{58,88}

Fig. 3 Densities, at $T = 298.15$ K and 0.1 MPa, as a function of the molar mass of the anion, M_{anion} . $\bullet$ – fluorinated ILs, $[C_4\text{mim}][\text{FAP}]$,⁸⁷ $[C_4\text{mim}][\text{Tf}_2\text{N}]$,⁷⁹ $[C_4\text{mim}][\text{PF}_6]$,⁷⁸ $[C_4\text{mim}][\text{BF}_4]$.⁸¹ $\blacklozenge$ – cyano-based ILs, $[C_4\text{mim}][\text{TCM}]$ (this work), $[C_4\text{mim}][\text{SCN}]$,⁵⁸ $[C_4\text{mim}][\text{DCA}]$ ^{58,88} and $[C_4\text{mim}][\text{TCB}]$.⁵⁶

studies, it was found that the density increases with increasing molar mass of the fluorinated anions, while a reverse trend is observed for the cyano-based anions. One of the explanations for these tendencies was the fact that the introduction of a fluorine atom has a strong influence on the molar weight of a molecule.⁵⁸ As explained above, the higher structural organization efficiency resulted from the higher dispersive interactions present in the fluorinated ILs leads to an increase of the density with increasing the molar weight/molar volume of the anion.

For the case of cyano-based ILs, the decrease of the density with the increase of the molar mass/molar volume of the anion is related to differences in structural organization, which are also depicted in RDFs calculated from molecular simulation^{17,53} (Fig. 4). In Fig. 4(I), the RDF between anion–cation centers of mass is shown for $[C_4\text{mim}][\text{TCM}]$ at 298 K in comparison to the

one of $[C_4\text{mim}][\text{Tf}_2\text{N}]$ with a slightly higher peak in the case of the fluorinated anion. This RDF curve implicitly accounts for the density of each IL system as well as the difference in the shape and size of the two anions. Moreover, the weaker ion pairing in case of $[C_4\text{mim}][\text{TCM}]$ is supported by quantum mechanical calculations on minimum energy configurations of an ion pair (as well as on a small ion cluster consisted of two ion pairs) that resulted in smaller mean total ionic charge (equal to $\pm 0.7355e$)⁵³ compared to the ones extracted in a similar manner for ion pairs for $[C_4\text{mim}][\text{Tf}_2\text{N}]$ (equal to $\pm 0.887e$).⁹¹

Furthermore, differences are observed for the case of anion–anion RDF, in which a first peak appears at short distances in the $[\text{TCM}]^-$ -based ILs, while for the cation–cation analysis a small peak at about 6 Å is observed. The tendency for chain aggregation phenomena is also slightly higher for this IL family (Fig. 4(IV)). Varying the alkyl chain length in the $[\text{TCM}]^-$ -based ILs, the anion–cation peak is less intense in $[C_2\text{mim}][\text{TCM}]$, increases in $[C_4\text{mim}][\text{TCM}]$ to decrease again in $[C_8\text{mim}][\text{TCM}]$.⁵³ In the $[\text{Tf}_2\text{N}]^-$ -based ILs, the anion–cation RDF does not follow the same behavior as in that case the peak of the anion–cation RDF decreases as the alkyl chain becomes longer.^{17,18}

Dynamic heterogeneity phenomena are detected in both ILs at 298 K, with the $[\text{TCM}]^-$ anion exhibiting a higher peak (at a timescale of 45 ps) in the non-Gaussian parameter than the one of the $[\text{Tf}_2\text{N}]^-$ anion (that preserves its high value from approx. 30 ps up to approx. 1 ns), while the inverse is observed for the cations in $[C_4\text{mim}][\text{TCM}]$ (maximum at approx. 80 ps) and $[C_4\text{mim}][\text{Tf}_2\text{N}]$ (maximum at approx. 120 ps) systems (Fig. 5).¹⁸ Generally, the microscopic structural characteristics, also between specific sites on the ions,^{17,53} reflect that the anion–cation interaction is less intense in the $[\text{TCM}]^-$ -based ILs and this fact along with $[\text{TCM}]^-$ anion shape and size allows a more uniform distribution of the anion around the cation compared to the fluorinated case, in which the $[\text{Tf}_2\text{N}]^-$ anion is preferentially located mostly at specific relative positions near the imidazolium ring.^{17,18,53} A representative example for the spatial distribution function of the central carbon in $[\text{TCM}]^-$ around the imidazolium ring of $[C_4\text{mim}]^+$ is shown in Fig. 6.

4.2 Viscosity

The experimentally determined dynamic viscosities of $[C_n\text{mim}][\text{TCM}]$ ILs, at atmospheric pressure, in the temperature range from 288.15 to 363.15 K, are listed in Table S3 (ESI†) and summarized in Fig. 7(I) together with the viscosities calculated *via* molecular simulations. The viscosities at $T = 298.15$ K as a function of the alkyl chain length are shown in Fig. 7(II). Molecular simulation captures well the temperature dependence of viscosity being in satisfactory agreement with experimental data, taking under consideration that viscosity is a collective property and is very difficult to reproduce in simulations. The deviations between the experimentally determined viscosities in this study and those reported in literature are shown in Fig. S2 (ESI†).

The experimentally determined viscosities of $[C_n\text{mim}][\text{TCM}]$ presented in this work are in good agreement with the literature data, within 2%, with the exception of $[C_2\text{mim}][\text{TCM}]$ reported

Fig. 4 Radial distribution function between (I) anion–cation center of mass; (II) anion–anion center of mass; (III) cation–cation center of mass; (IV) terminal carbon atoms; for $[C_4mim][TCM]$ (solid black line) and $[C_4mim][Tf_2N]$ (dash-dotted red line).

Fig. 5 Non-Gaussian parameter $\alpha_2(t)$ for (I) $[TCM]^-$ anion (solid black line) and the $[Tf_2N]^-$ anion (dash-dotted red line) and (II) of $[C_4mim][TCM]$ cation (solid black line) and $[C_4mim][Tf_2N]$ cation (dash-dotted red line), calculated at 298.15 K.

by Yoshida *et al.*⁷⁶ (12% at 295.15 K) and Ganbold *et al.*,⁹² (16 and 26% between 298 and 333 K). The higher deviations can be related to iodide and other impurities originated from the synthesis.⁹³ A systematic error with a maximum deviation of

7.8% is observed for the data ($[C_nmim][TCM]$, $n = 2$ and 4) published by Bi *et al.*,⁵⁷ which could result from the different experimental technique used.⁵⁷ No literature data were found for $[C_7mim][TCM]$.

Fig. 6 Spatial distribution function of the central carbon in [TCM][−] anion around the imidazolium ring of [C₄mim]⁺ cation at 298.15 K using an iso-surface value equal to 5.4 nm^{−3}.

The viscosities of the [TCM][−]-based ILs were correlated with the Vogel–Fulcher–Tammann (VFT) model:

$$\eta(T) = A_{\eta} \exp \left[\frac{B_{\eta}}{(T - C_{\eta})} \right] \quad (6)$$

where $\eta(T)$ is the viscosity in mPa s, T is the temperature in K, and A_{η} , B_{η} and C_{η} are adjustable parameters. The derived parameters of VFT equation obtained in this work are listed in Table S4 (ESI[†]). The correlated viscosities are in excellent agreement with the experimental data, with a maximum relative deviation of 0.2%.

Viscosity relates the internal resistance of a fluid to shear stress, which is associated with intermolecular interactions. ILs usually display higher viscosities than common molecular solvents,^{11,80} mainly due to their configurational arrangement and charge distribution, which involves not only Coulombic interactions, but also van der Waals interactions and hydrogen bonding. The energy barrier of the fluid to shear stress, E , can

be evaluated based on the viscosity dependence with the temperature using eqn (7):^{94,95}

$$E = R \left[\frac{\partial(\ln[\eta(T)])}{\partial\left(\frac{1}{T}\right)} \right]_p = R \frac{B_{\eta}}{\left(\frac{C_{\eta}^2}{T^2} - \frac{2C_{\eta}}{T} + 1\right)} \quad (7)$$

where R is the gas constant ($R = 8.3144621 \text{ J K}^{-1} \text{ mol}^{-1}$).⁹⁶ The energy barrier values, E , at $T = 298.15 \text{ K}$, for the [TCM][−]-based ILs are listed in Table S4 (ESI[†]), and are represented together with the pre-exponential coefficient, A_{η} , of the VFT equation (eqn (6)) in Fig. S3 (ESI[†]).

A linear increase of the viscosity with increasing alkyl chain length of the imidazolium cation is observed, which is in agreement with the higher resistance to the flow due to the increase of the dispersive interactions and the increase of the size/entanglement of the alkyl chains. This behavior was observed for other IL families (Fig. 8).^{11,78,79} In literature reporting thermophysical data for imidazolium based ILs, several trends were detected on the properties, a fact that reflects the complexity of the structural organization and molecular interactions in the bulk liquid.^{78,79,97,98} However, there is limited molecular understanding of the structural organization and dominance of the specific intermolecular interactions in ILs containing cyano-anions, which challenges a deeper analysis of the effect of the anion on structure–property relationships. The increase of the viscosity with the increase of the alkyl chain length is in agreement with the decrease of diffusivity (see Section 4.5) and the increase of the energy barrier, which is related to the increase of the intermolecular interactions. A decrease of the pre-exponential parameter of the VFT eqn (6), A_{η} , upon increasing of the alkyl chain length is observed due to a decrease of the surface-to-volume ratio of the ion pairs.

In this work, a linear increase of the viscosity with the alkyl chain length of the imidazolium cation is observed. Since in

Fig. 7 (I) Viscosity as a function of temperature for the studied ILs. Experimental data: ◀ – [C₂mim][TCM]; ◆ – [C₄mim][TCM];¹ ● – [C₆mim][TCM]; ■ – [C₇mim][TCM]; ▲ – [C₈mim][TCM]. Simulation data: ◁ – [C₂mim][TCM]; ◇ – [C₄mim][TCM]; ○ – [C₆mim][TCM]; △ – [C₈mim][TCM]. The solid lines represent the values calculated using the Vogel–Fulcher–Tammann fitting parameters (eqn (6)). (II) Viscosity at $T = 298.15 \text{ K}$ and 0.1 MPa as function of the number of carbons of the alkyl chain, $n(C)$, for [C_{*n*}mim][TCM] ILs. The symbols represent experimental data and the line is intended as a guide for the eye.

Fig. 8 Plots of: (I) viscosity at 298.15 K as a function of the number of carbons on the alkyl chain of the cation, $n(C)$, for several IL series; (II) zoom in on the viscosities of the cyano-based ILs. This work: $\blacktriangle$ – $[C_n\text{mim}][\text{TCM}]$ ($n = 2, 4$ and $6-8$). Literature: $\bullet$ – $[C_n\text{mim}][\text{Tf}_2\text{N}]$ ($n = 2-10$);^{79,100} $\blacklozenge$ – $[C_n\text{mim}][\text{PF}_6]$ ($n = 4-9$);⁷⁸ $\blacktriangleleft$ – $[C_n\text{mim}][\text{BF}_4]$ ($n = 2, 3, 6$ and 8);^{101,102} $\blacklozenge$ – $[C_n\text{mim}][\text{TCB}]$ ($n = 2, 4$ and 6);^{57,58} $\bullet$ – $[C_n\text{mim}][\text{DCA}]$ ($n = 2, 4$ and 6).^{58,88}

this study only the ILs with an even number of carbon atoms ($n = 2-8$) together with $[C_7\text{mim}][\text{TCM}]$ is explored, the effect of the nano-segregation on the properties in this family of ILs is not clear. The influence of the anion on the viscosities at 298.15 K against the carbon number ($n(C)$) of the alkyl chain of imidazolium-based ILs can be observed in Fig. 8(I).

The effect of the anion (fluorinated and non-fluorinated) on the pre-exponential coefficient, A_η , and the energy barrier, E , of the ILs are shown in the Fig. S4 and S5 (ESI†). As expected, the $[\text{PF}_6]^-$ -based ILs display the highest viscosity of all the ILs series, as a result of the stronger intermolecular interactions.⁷⁸ The contribution per $-\text{CH}_2-$ group to the increase of the viscosity presents the following sequence: $[\text{PF}_6]^- > [\text{BF}_4]^- > [\text{Tf}_2\text{N}]^- > [\text{DCA}]^- > [\text{TCB}]^- > [\text{TCM}]^-$. This trend is consistent with MD simulations.⁵² As the size of the fluorinated anions increases, the viscosity decreases (higher molecular motion). This is related to the reduction of the electrostatic interactions and an increase of the more flexible polar region.^{58,99} This trend is not observed for the cyano-based ILs. Instead, an irregular behavior is found,

in which the $[\text{TCM}]^-$ -based ILs (intermediate number of $-\text{CN}$ groups) has the lowest viscosity of all the considered cyano-based ILs. This is in agreement with the findings of Neves *et al.*⁵⁸

Another interesting aspect is the fact that both $[\text{DCA}]^-$ and $[\text{TCB}]^-$ -based ILs show a higher increase in the viscosity with increasing alkyl chain length compared to the $[\text{TCM}]^-$ -based ILs, see Fig. 8(II). Furthermore, at 298.15 K the order shown at $[C_2\text{mim}]^+$ cation is not maintained when the alkyl chain of the cation increases except for the $[\text{TCM}]^-$ -based ILs. At C_6 the order is reversed whereby the $[\text{DCA}]^-$ IL has a slightly higher viscosity than the $[\text{TCB}]^-$ IL. Moreover, this cross-over is also influenced by the temperature as can be seen in Fig. 9, where the viscosities at C_2 and C_6 are displayed as a function of temperature. The longer the alkyl chain, the lower the temperature at which the shift takes place (C_2 at approx. 328 K, (C_4 at approx. 308 K, not shown here) and C_6 at approx. 298 K).

The pre-exponential coefficient, A_η , of the VFT eqn (6) and the energy barrier, E , (eqn (7)) for the cyano-based ILs, are represented in Fig. 10. The value of $[C_4\text{mim}][\text{B}(\text{CN})_4]$ has a high

Fig. 9 Viscosity as a function of temperature for the cyano-based ILs. (I) $[C_2\text{mim}]^+$ and (II) $[C_6\text{mim}]^+$ ILs. This work: $\blacktriangle$ – $[\text{TCM}]^-$. Literature $\blacktriangledown$ – $[\text{TCB}]^-$;^{57,58} $\bullet$ – $[\text{DCA}]^-$.⁵⁸ The viscosities represented obtained using the same experimental technique.

uncertainty mainly due to the methodology used in the viscosity measurements.⁵⁵ Therefore, the analysis will focus on the $[\text{C}_2\text{mim}]^+$ and $[\text{C}_6\text{mim}]^+$ cations. The pre-exponential value decreases in the following order: $[\text{DCA}]^- > [\text{TCM}]^- > [\text{TCB}]^-$. For the ILs with $[\text{C}_6\text{mim}]^+$ cation, a change in the A_η order is observed, decreasing from $[\text{TCM}]^-$ to $[\text{DCA}]^-$. On the other hand, the energy barrier increases with increasing the number of $-\text{CN}$ groups in the anion and upon increasing the alkyl chain of the cation. The lower viscosity of the $[\text{TCM}]^-$ -based ILs cannot be clearly explained by the pre-exponential factor or the energy barrier values. The lower viscosity can be directly connected to the existence of a strong charge delocalization and a smaller electronegativity in $[\text{TCM}]^-$ -based ILs leading to weaker ion pairing and to a higher fluidity and lower melting temperatures.^{53,103}

4.3 Surface tension

The measured surface tension, γ , data of $[\text{C}_n\text{mim}][\text{TCM}]$ are given in Table S5 (ESI[†]) and are depicted in Fig. 11 together with the simulation results. For each data point five measuring runs were performed with at least three individual temperature and Wilhelmy plate surface tension readings per run. A platinum plate is chosen as it is chemically inert, easy to clean and because its high surface free energy results in optimal wetting (contact angle θ is 0° with liquids). During the course of the measurements, as a result of the hygroscopic nature of the $[\text{TCM}]^-$ -based ILs, the water content increased. The moisture mass fractions after the first and the last measurement are included in Table S5 (ESI[†]).

Generally, the surface tension decreases with increasing alkyl chain length for imidazolium-based ILs.¹⁰⁴ Koller *et al.*¹⁰⁵ and Almeida *et al.*¹⁰⁶ found the same pattern for the homologous series of the $[\text{TCM}]^-$ -based ILs, *i.e.* decreasing surface tension upon increasing alkyl chain length. However, in this work a peculiarity is observed. At a certain temperature, the surface tension of the investigated ILs decreases in the following order: $[\text{C}_4\text{mim}][\text{TCM}] > [\text{C}_2\text{mim}][\text{TCM}] > [\text{C}_6\text{mim}][\text{TCM}] > [\text{C}_7\text{mim}][\text{TCM}] > [\text{C}_8\text{mim}][\text{TCM}]$, see Fig. 11. This trend was also detected by

Fig. 11 Surface tension of the $[\text{C}_n\text{mim}][\text{TCM}]$ ILs as function of temperature. Closed symbols represent the experimental measurements and open symbols represent simulation data. $\blacktriangle$ – $[\text{C}_2\text{mim}][\text{TCM}]$; $\blacklozenge$ – $[\text{C}_4\text{mim}][\text{TCM}]$; $\bullet$ – $[\text{C}_6\text{mim}][\text{TCM}]$; $\blacksquare$ – $[\text{C}_7\text{mim}][\text{TCM}]$; $\blacktriangle$ – $[\text{C}_8\text{mim}][\text{TCM}]$. The solid lines represent the values calculated using eqn (8).

Součková *et al.*¹⁰⁷ ($[\text{C}_2\text{mim}][\text{TCM}]$ and $[\text{C}_4\text{mim}][\text{TCM}]$ are the only imidazolium- $[\text{TCM}]$ ILs reported) using the Wilhelmy plate method and the du Noüy ring method.

Surface tension data published by different groups for the $[\text{TCM}]^-$ -based ILs with an imidazolium ring, show noticeable differences. This has been also reported by others.^{106,107} The deviations between the experimental results in this study and those found in literature are shown in Fig. S6 (ESI[†]) and are presented in Table 2. The molecular simulations also suggest a monotonic behavior for the surface tension of the homologous series with the alkyl chain length. Nevertheless, despite the large standard deviations in the predicted values (varying between 1.2 mN m^{-1} at low temperatures and 3.6 mN m^{-1} at high temperatures) simulation results are in reasonable agreement with the present experiments for the ILs. Additionally,

Fig. 10 (I) Pre-exponential coefficient ($A_\eta/\text{mPa s}$) of the VFT eqn (6) and (II) energy barrier ($E/\text{kJ mol}^{-1}$) (eqn (7)) at $T = 298.15 \text{ K}$ as function of the number of carbon atoms in the alkyl chains, $n(\text{C})$, for the cyano-based ILs. This work: $\blacktriangle$ – $[\text{C}_n\text{mim}][\text{TCM}]$ ($n = 2, 4$ and $6-8$). Literature $\bullet$ – $[\text{C}_n\text{mim}][\text{TCB}]$ ($n = 2, 4$ and 6),^{57,58} $\bullet$ – $[\text{C}_n\text{mim}][\text{DCA}]$ ($n = 2, 4$ and 6).^{58,88}

Table 2 Percent absolute average relative deviations (AARD%) calculated for the surface tension between the experimentally determined values in this work and the data reported in literature and molecular simulation results

IL	AARD (%)	Source (method)	No. of data points
[C ₂ mim][TCM]	8.3	Koller <i>et al.</i> ¹⁰⁵ (pendant drop method)	5
	11.1	Almeida <i>et al.</i> ¹⁰⁶ (pendant drop method)	6
	6.7	Součková <i>et al.</i> ¹⁰⁷ (Wilhelmy plate method)	10
	2.4	Molecular simulation	4
[C ₄ mim][TCM]	3.6	Koller <i>et al.</i> ¹⁰⁵ (pendant drop method)	5
	5.8	Almeida <i>et al.</i> ¹⁰⁶ (pendant drop method)	6
	6.2	Součková <i>et al.</i> ¹⁰⁷ (Wilhelmy plate method)	10
	4.8	Molecular simulation	4
[C ₆ mim][TCM]	3.6	Koller <i>et al.</i> ¹⁰⁵ (pendant drop method)	5
	1.3	Molecular simulation	4
[C ₈ mim][TCM]	7.7	Koller <i>et al.</i> ¹⁰⁵ (pendant drop method)	5
	1.5	Molecular simulation	4

they are generally in better agreement with the experiments than the individual experimental studies among themselves.

The disparities among the experimental studies may be caused by various factors. For instance, different methods used by the individual groups, the impurities in the sample and the susceptibility to water affect the measurements. The suitability of the experimental method used and the appropriate handling has been verified by comparing measured data of three different (standard) solvents (water, toluene and diisodecyl phthalate) at different temperatures with reported data in literature,^{108–110} see Table S6 (ESI[†]). The measured values are in excellent agreement with data from literature. Moreover, Koller *et al.*¹⁰⁵ have performed experiments with the ILs provided by the same supplier (IoLiTec) with the same specifications (although not from the same batch). Therefore, the impurities should not play a role when comparing the results of this work with their data. The [TCM][−]-based ILs are hygroscopic and hydrophilic as has already been shown in one of our previous works.² Despite the fact that some investigators¹¹¹ have indicated that water has a negligible effect on the surface tension, it is important, in all cases, but especially with hydrophilic ILs to report the water content, since most of the thermophysical properties are affected by the presence of water.^{2,112,113} In our previous study,² it has been shown that water disrupts the anion–cation interactions through the formation of hydrogen bonds between water and the [TCM][−] anions leading to a positive excess molar volume and negative viscosity deviations for the binary systems. In addition, growth of water clusters within the ILs polar network would further separate the anions and weakens the electrostatic interactions even more, resulting in a non-monotonous variation in physical properties (*e.g.* density and viscosity).¹¹⁴ Freire *et al.*¹¹³ have studied the effect of water on the surface tension and observed a decrease for low water content, which was more pronounced for the more hydrophilic ILs. At higher water contents, when complete solvation of the ions has been reached, further hydrogen bonding is not possible, leading to a new structural rearrangement, which results in an increase in the physical properties such as the surface tension.^{93,115} MD simulations performed to calculate the surface tension of the pure ILs suggest a higher cation number

density near the surface. Both water molecules and anions compete to be in the vicinity of the cation, therefore water is expected to have a strong presence in the surface, leading to a decrease in the overall cohesive energy due to lower electrostatic interactions, and subsequently, to lower surface tension values. Based on the findings stated above and the fact that the surface tension values of this work are systematically lower than the literature data, it can be concluded that the water content is one of the main sources of the deviations. Therefore, experimental data reported by different investigators are not comparable without taking into account the impurities and water content. The influence of water on surface tension of this particular IL family must be further investigated in terms of complex formations (H-bonds) and the surface excess concentration of water in the salt-rich region.

Furthermore, the measured surface tensions are distinctly higher than those of [Tf₂N][−]-based ILs at small to medium-sized alkyl chains and the difference drops with increasing alkyl chain, which is also evident from the difference in slopes between that of the [TCM][−]-based ILs and the [Tf₂N][−]-based ILs, see Fig. 12. ILs with perfluorinated anions such as [Tf₂N][−]-based ILs exhibit lower surface tension which is attributed to their size and shape as well as to their preferential orientation of the anions on the surface with the CF₃ groups oriented towards the vacuum.¹¹⁶ Within the group of smaller and more symmetrical anions, slightly higher surface tension values are observed for the [TCM][−]-based ILs compared to those of [TCB][−]-based ILs possibly due to the smaller size of the former anion which also affects the spatial organization on the surface. From the measured homologous series only [C₂mim][TCM] shows a lower surface tension compared to [C₂mim][BF₄] and [C₂mim][PF₆]. According to Koller *et al.*¹⁰⁵ this might be due to higher presence of charged groups at the surface resulting in a large impact of the Columbic interactions, which are stronger for shorter the alkyl chain, on the surface tension.

4.3.1 Surface thermodynamics. The experimentally determined surface tension values vary (quasi) linearly with the temperature within the range they are measured. The surface enthalpy, H^A , and the surface entropy, S^A , are derived respectively from the

Fig. 12 Surface tension at 298.15 K as function of the number of carbons of the alkyl chain, $n(\text{C})$, for $[C_n\text{mim}][\text{TCM}]$ ILs (●) compared to selected families of ILs: ◆ – $[C_n\text{mim}][\text{Tf}_2\text{N}]$ Carvalho *et al.*,¹¹³ ▲ – $[C_n\text{mim}][\text{PF}_6]$ Klomfar *et al.*,¹¹⁷ ▼ – $[C_n\text{mim}][\text{TCB}]$ Koller *et al.*,¹⁰⁵ □ – $[C_n\text{mim}][\text{BF}_4]$ Xu *et al.*,¹¹⁸ ● – $[C_n\text{mim}][\text{TCM}]$ Koller *et al.*¹⁰⁵

intercept and the slope of the linear relationship between the surface tension and temperature:¹¹⁹

$$H^A = \gamma - T \left(\frac{d\gamma}{dT} \right)_P \quad (8)$$

$$S^A = - \left(\frac{d\gamma}{dT} \right)_{A,P} \quad (9)$$

The determined values of H^A and S^A and their respective uncertainties are presented in Table S7 (ESI†). The surface enthalpy and entropy of the studied ILs are compared with the selected families of ILs in Fig. 13. A decrease of the surface enthalpies with increasing alkyl chain of the cation is detected

for all ILs except for the $[C_n\text{mim}][\text{Tf}_2\text{N}]$ series. Concerning the surface entropy, only the $[\text{TCM}]^-$ -based ILs of this work show a clear decreasing trend with increasing alkyl chain length, while $[\text{BF}_4]^-$ - and $[\text{Tf}_2\text{N}]^-$ -based ILs display a slight increase upon increasing the alkyl chain length. Moreover, the fluorinated ILs show lower surface entropies compared to the cyano-based ILs, which is related with the higher surface organization. This is consistent with the findings stated above.

These trends in surface enthalpy and entropy suggest a higher surface organization in $[\text{TCM}]^-$ -based ILs than in $[\text{TCB}]^-$ -based ILs and it enhances with increasing alkyl chain length. At $[C_8\text{mim}]^+$ the $[\text{TCM}]^-$ -based ILs have a comparable surface organization as the $[\text{Tf}_2\text{N}]^-$ -based ILs. $[C_2\text{mim}][\text{TCM}]$ shows an outlier behavior relative to the rest of the homologous series. The obtained surface enthalpies for $[C_2\text{mim}][\text{TCM}]$ and $[C_4\text{mim}][\text{TCM}]$ are comparable, reflecting an interplay between the decrease in electrostatic interactions and the increase in the dispersive forces due to the increase of the alkyl chain length. Additionally, the similar surface entropy for both ILs suggests comparable surface organization. Starting from $[C_4\text{mim}][\text{TCM}]$, the ILs show a decrease of the surface thermodynamic properties. The observed decrease in the surface entropy with increasing the alkyl chain length for $[\text{TCM}]^-$ -based ILs could be related with the lower differentiation of structural organization between the surface and the bulk region.

The cyano-based ILs combined with imidazolium cations show surface enthalpies within the same range and surface entropies to some extent lower than molecular organic solvents¹²⁰ (Table S8, ESI†). However, it should be taken into account that surface thermodynamic properties, such as other properties, highly depend on the structural and chemical nature of the compound and general conclusions should be avoided.

4.4 Electrical conductivity

The application of ILs as electrolytes in electrochemistry,¹²² fuel cells,¹²³ electrochemical devices,⁸ such as rechargeable

Fig. 13 (I) Surface enthalpy and (II) surface entropy as function of the number of carbons of the alkyl chain, $n(\text{C})$, for $[C_n\text{mim}][\text{TCM}]$ ILs (●) compared to selected families of ILs: ◆ – $[C_n\text{mim}][\text{Tf}_2\text{N}]$ Carvalho *et al.*,¹²¹ ▲ – $[C_n\text{mim}][\text{PF}_6]$ Klomfar *et al.*,¹¹⁷ ▼ – $[C_n\text{mim}][\text{TCB}]$ Koller *et al.*,¹⁰⁵ □ – $[C_n\text{mim}][\text{BF}_4]$ Xu *et al.*,¹¹⁸ ● – $[C_n\text{mim}][\text{TCM}]$ Koller *et al.*¹⁰⁵

lithium batteries¹²⁴ rely for a large extent on ionic conductivity. Therefore it is important to understand the factors influencing the conductivity. Electrical conductivities, κ , of [C_nmim][TCM] were studied in the temperature range from 293.25 to 379.25 K at atmospheric pressure. This property depends on the number of charge carriers, the charge and the mobility of the species according the following equation:¹²⁵

$$\kappa = \sum n_i q_i u_i \quad (10)$$

where n_i is the number density (m⁻³) of charge carriers of type i , q_i is the charge (C) and u_i is the mobility (m² V⁻¹ s⁻¹) of species i , which is related to the viscosity of the fluid. Hence, conductivities of ILs increase significantly with temperature due to a decrease of the viscosity. The temperature dependence of [C_nmim][TCM] electrical conductivity is illustrated in Fig. 14 and given in Table S9 (ESI†). To the best of our knowledge, there are no systematic studies of the electrical conductivity data for the [TCM]⁻-based ILs reported in literature, except for [C₂mim][TCM] by Yoshida *et al.*⁷⁶ and Ganbold *et al.*¹²⁶ As already observed for the viscosities reported by the two groups the data significantly deviate from the measured values reported in the present work. The conductivities deviate by 27%⁷⁶ and between 55 and 72%¹²⁶ and are therefore not included here for a comparison study. The ionic conductivity can be estimated assuming an uncorrelated contribution of the individual species to the total ionic conductivity using the Nernst-Einstein (NE) equation:

$$\sigma_{\text{NE}} = \frac{N_{\text{pairs}}}{3Vk_B T} (q_+^2 D_+ + q_-^2 D_-) \quad (11)$$

with N_{pairs} equal to the number of the ion pairs in the system (m⁻³), V the volume (m³), q the ionic charge (C) and D_+ and D_- are the anion and cation diffusion coefficients (m² s⁻¹), respectively. Ionic conductivity was extracted using the Nernst-Einstein relation (eqn (11)) based on the ions' self-diffusivities computed from molecular simulations (Section 4.5). The conductivity decreases

with increasing chain length. This phenomenon could be explained by the mobility of the charge carriers which decreases with increasing viscosity, see Fig. 7(I). The higher viscosity is caused by the larger cation size and the stronger van der Waals interactions between the longer alkyl chains.¹²⁷ The observed temperature dependence of electrical conductivity is often described by the empirical VFT equation:¹²⁸

$$\kappa(T) = \kappa_0 \exp \left[\frac{-B}{T - T_0} \right] \quad (12)$$

where κ_0 (mS cm⁻¹), B (K) and T_0 (K) are the fitting parameters. B is related to the activation energy and T_0 is a factor related to the ideal glass transition temperature. The best-fit parameters and the correlation coefficients are given in Table S10 (ESI†). This form of the empirical VFT equation is normally used to describe the temperature dependence of the structural relaxation time and the conductivity of supercooled liquids and glass forming systems. The [TCM]⁻-based ILs belong to the latter group. Determination of the relaxation time and the glass transition temperature are beyond the scope of the current work.

4.4.1 Walden plot: conductivity-viscosity relationship. The relationship between molar conductivity and viscosity is analyzed using the empirical fractional Walden rule:¹²⁹

$$A\eta^\alpha = C(T) \quad (13)$$

where C is a temperature-dependent constant, α is the slope of the line in the Walden plot, which reflects the decoupling of the ions and A is the molar conductivity given by:

$$A = \kappa V_m = \kappa \frac{M}{\rho} \quad (14)$$

where V_m is the molar volume, and M is the molar mass of the IL. Fig. 15(I) shows the linear relationship between the molar conductivities and the viscosities of the [TCM]⁻-based ILs. The value of the slope (α) is 0.64, 0.68, 0.75 and 0.78 for [C₂mim][TCM], [C₄mim][TCM], [C₆mim][TCM] and [C₈mim][TCM], respectively. In all cases R -squared is better than 0.998. The linear correlation in the Walden plot clearly shows the coupling of the IL conductivity and viscosity.⁵ Furthermore, one of the main advantages of plotting molar conductivities (A) instead of the absolute conductivities (κ), is that the former partially normalizes the effect of density and molar concentration and hence gives a better indication of the number of mobile charges in an IL.⁵ Besides, with the obtained fitting parameters, one of the properties (either viscosity or conductivity dependent on the availability) can reliably be calculated from the experimentally obtained data of the other property. The straight line in Fig. 15(I) that passes through the origin is generated from the data of a 0.01 M KCl solution (fully dissociated) that provides a useful calibration point and serves as a reference line in the Walden plot.¹³⁰ Most of the ILs fall well below this reference line, apparently because of ion association in its different forms (e.g. ion-ion correlations and aggregates), which could be responsible for the decrease in number of effective charge carriers.^{131,132} Ion pairs and groups or aggregates of ions, when long-lived, contribute less to conductivity, because they appear neutral in the electric field.¹³³ As it can be seen in Fig. 15(I) the [TCM]⁻-based ILs

Fig. 14 Electrical conductivity of [C_nmim][TCM] as function of temperature. The symbols are the experimental data (closed symbols) and molecular simulation estimations (open symbols) (◆ – [C₂mim][TCM]; ▲ – [C₄mim][TCM]; ● – [C₆mim][TCM]; ▲ – [C₈mim][TCM]) and the solid line is the fit using eqn (12).

Fig. 15 (I) Walden plot of [TCM][−]-based ILs and a selection of ILs with a common cation ([C₂mim]⁺) and different anions, where Λ is the molar conductivity and η^{-1} is the fluidity. The filled symbols represent the experimental data of the present work: (◆ – [C₂mim][TCM]; ▲ – [C₄mim][TCM]; ● – [C₆mim][TCM]; ▲ – [C₈mim][TCM]). Literature: Schreiner *et al.*¹²⁹ (● – [C₂mim][BF₄]; ■ – [C₂mim][Tf₂N]; ▲ – [C₂mim][DCA]). The ideal line (solid black) represents the 0.01 M KCl line. (II) Adjusted Walden plot of [TCM][−]-based ILs, where Λ is the molar conductivity, η^{-1} is the fluidity and r^{+} and r^{-} are the respective cation and anion sizes. The symbols are the experimental data (◇ – [C₂mim][TCM]; < – [C₄mim][TCM]; ○ – [C₆mim][TCM]; △ – [C₈mim][TCM]). The ideal line (solid black) represents the 0.01 M KCl line.

are also below the ideal line. Furthermore, the longer the alkyl chain length, the lower the Walden product. It has already been observed that the Walden product varies inversely with the ion size.¹³⁴

The general Walden plot (Fig. 15(I)) represents a qualitative tool for estimating the ionicity, effective fraction of ions that contribute to conduction, of ILs based on two easily measurable quantities. However, it does not explicitly take into account the differences in ion size. Therefore, an adjusted form of the Walden plot, which takes into account the radii of the cation and the anion, provides more insight into the ionicity of the ILs. When self-diffusion data are available, the Nernst–Einstein equation (eqn (11)) can be applied.^{135,136} In cases where the diffusion measurements are not available, the ion size can be deduced from the Stokes–Einstein equation as suggested by Bonhote *et al.*¹³⁷ and Abbott.¹³⁸ The Stokes–Einstein equation reads:

$$D_i = \frac{k_B T}{6\pi\eta r_i} \quad (15)$$

where D_i is diffusion coefficient of component i . When substituted into the Nernst–Einstein equation (eqn (11)) for a 1:1 salt, yields:

$$\Lambda = C\eta^{-1} \left(\frac{1}{r^{+}} + \frac{1}{r^{-}} \right) \quad (16)$$

where r^{+} and r^{-} are the ‘effective’ cation and anion radii, respectively. In the present work, these effective sizes were extracted from the ion volume as calculated on minimized isolated ion structures¹³⁹ under the assumption of a spherical ion shape that is expected to underestimate the true hydrodynamic radii.

The adjusted Walden plot where $\log \Lambda$ is plotted vs. $\log \eta^{-1} ((1/r^{+}) + (1/r^{-}))$ is depicted in Fig. 15(II). The radii are presented in Table S11 (ESI[†]). This modification decreases the deviation between the ILs and the ideal 0.01 M KCl line and improves its qualitative nature.¹³³ Angell *et al.*¹³⁰ denotes this deviation

as ΔW . A ΔW equal to unity specifies an ionic conductivity of only 10% of the 0.01 M KCl solution. For the [TCM][−]-based ILs, ΔW varies between 0.13 ([C₂mim][TCM] at 298.15 K) and 0.46 ([C₈mim][TCM] at 363.15 K). ILs with similar ionicity, within one order of magnitude from the ideal line, could be classified as good or (high ionicity) ILs.¹³⁰ This suggests that the ILs within this range are composed of practically independent mobile ions. The influence of the anion on the interdependence of ionic conductivity and viscosity is further investigated by comparing different ILs having the same cation, *i.e.* [C₂mim]⁺.¹²⁹ The deviations (ΔW) from the ideal line at 298.15 K follow the trend: [BF₄][−] > [Tf₂N][−] > [TCM][−] > [DCA][−]. [TCM][−]-based ILs show larger temperature dependence than the other ILs.

In the adjusted Walden plot ΔW is significantly reduced (see Table S12, ESI[†]) suggesting an enhanced ionicity. This improvement underlines once more the qualitative nature of the Walden plot.

4.5 Self-diffusion coefficients

The self-diffusion coefficients, D_{self} , of the cations [C_{*n*}mim]⁺ ($n = 2, 4, 6$ and 8) are shown in Fig. 16 as a function of temperature. Molecular simulation predictions for the diffusivity coefficients for both the anion and the cations were obtained in the temperature range from 300 to 366 K. The self-diffusion coefficients of the cations are in good agreement with the experimental results (no experimental data are currently available for the diffusivity of the anions). Table S13 (ESI[†]) includes the experimental data and molecular simulation calculations as a function of temperature. As one can observe, the self-diffusion of the cations decreases with increasing alkyl chain attached to the imidazolium ring. The dependence of self-diffusion on the alkyl chain length shows that the ion size is an important factor controlling the diffusion of ions. The increase of the alkyl chain

Fig. 16 Self-diffusion coefficients of the cations in $[C_n\text{mim}][\text{TCM}]$ ILs, ($n = 2, 4, 6$ and 8) at 0.1 MPa as a function of temperature. The closed symbols represent experimental data (● – $[\text{C}_2\text{mim}]^+$; ▼ – $[\text{C}_4\text{mim}]^+$; ■ – $[\text{C}_6\text{mim}]^+$; ▲ – $[\text{C}_8\text{mim}]^+$) and the open symbols represent the molecular simulation results.

length increases the dispersive interactions between the alkyl chains in the liquid phase that results to chain aggregation phenomena for the longer alkyl chains, whereas it has a lesser effect on the interaction energy between the cation and the anion.¹⁴⁰ This trend was expected based on the temperature dependence of the viscosity (Fig. 7(I)), which shows opposite profiles indicating an inverse relationship between viscosities and self-diffusion coefficients. The interrelation between the two properties can be explained especially at higher temperatures in terms of the Stokes–Einstein equation (eqn (15)).

In general, molecular simulation predictions often strongly underestimate self-diffusion coefficients.¹⁴¹ Predicted self-diffusivities in this work are in good agreement compared to the experimental values (see Fig. 16 and Table S13, ESI†). For the shorter alkyl chains, the anion and the cation have comparable diffusivities, but as the alkyl chain becomes longer (and the cation heavier), the anion becomes more mobile than the cation.⁵³ This was also observed in experimental and molecular simulation studies on $[C_n\text{mim}][\text{TF}_2\text{N}]$ ILs.^{18,136} In a self-consistent manner, the less viscous $[\text{TCM}]^-$ -based ILs exhibit higher diffusivities than the corresponding $[\text{TF}_2\text{N}]^-$ ILs. The dynamical behavior of the IL systems under study are significantly affected in case of confinement.¹⁴² Due to the lack of experimentally determined self-diffusion coefficients of $[\text{TCM}]^-$ -based ILs and scarcity of the cyano-based systems in general, we are constrained to compare only to the $[\text{C}_2\text{mim}][\text{TCB}]$ system investigated by Koller *et al.*¹⁴³ The comparison shows that the self-diffusion coefficients of the $[\text{C}_2\text{mim}]^+$ cation in $[\text{C}_2\text{mim}][\text{TCM}]$ is higher than in $[\text{C}_2\text{mim}][\text{TCB}]$ ($8.64 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ vs. $5.81 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ at 298.15 K). This could be explained by the fact that the $[\text{TCM}]^-$ anion is lighter compared to the $[\text{TCB}]^-$ anion (90.06 g mol^{-1} and $114.88 \text{ g mol}^{-1}$, respectively) and the weaker intermolecular interactions between the cation and the anion in the $[\text{C}_2\text{mim}][\text{TCM}]$ IL. This is in agreement with the findings stated above.

5 Conclusions

A thorough study of the thermophysical properties of the low-viscosity $[\text{C}_n\text{mim}][\text{TCM}]$ ($n = 2, 4$ and $6-8$) ILs has been presented. A comparison between the studied thermophysical properties with the available literature data is shown. The analysis is not limited to $[\text{TCM}]^-$ -based ILs, but includes other cyano- and fluorinated ILs. The latter are widely studied for their attractive properties (*e.g.* thermal and chemical stability and relative low viscosity). Therefore, in this work the structure–property relationship of the cyano-based ILs is extensively discussed using both experimental data and molecular simulation results. As expected, the densities of the $[\text{TCM}]^-$ -based ILs decrease with increasing temperature. Additionally, a decrease of the densities with increasing alkyl chain length of the imidazolium cation is observed. The effect of the anion on the densities of 1-alkyl-3-methylimidazolium based ILs is evaluated. For ILs with cyano anions the density decreases with increasing molar mass. This is related to differences in the structure observed in RDFs calculated from molecular simulations. $[\text{C}_4\text{mim}][\text{TCM}]$ exhibits a weaker ion pairing that is also supported by quantum mechanical calculations that resulted in a smaller total ionic charge compared to the ones extracted in a similar manner for the $[\text{C}_4\text{mim}][\text{TF}_2\text{N}]$ system. The fluorine-based ILs show higher densities than the ones containing cyano-anions, a fact that could be partially attributed to the contribution of the heterogeneous and heavy atoms. In addition, the shape/symmetry and strong ionic interactions of fluorine-based ILs enhances a more selective distribution around the charged cation. This can be related to a higher structural organization in the bulk liquid, leading to higher densities. Moreover, compared to the cyano-based ILs, a reverse trend is observed for ILs with fluorinated anions, that is the density increases with increasing molar mass.

Both $[\text{DCA}]^-$ - and $[\text{TCB}]^-$ -based ILs show a higher increase in the viscosity with increasing alkyl chain length compared to the $[\text{TCM}]^-$ -based ILs. Furthermore, $[\text{DCA}]^-$ - and $[\text{TCB}]^-$ -based ILs show a switch in the viscosity with increasing the alkyl chain length of the cation, which is influenced also by the temperature. The lower viscosity of the studied $[\text{TCM}]^-$ ILs could be connected with the more uniform distribution of the anion around the cation contributing to a higher fluidity as a result of the weaker anion–cation interaction. A higher viscosity is observed for fluorinated ILs, which decreases as the size of the fluorinated anions increases.

The surface tension decreases with increasing the alkyl chain length of the $[\text{C}_n\text{mim}][\text{TCM}]$ IL series, with the exception of $[\text{C}_2\text{mim}][\text{TCM}]$ that exhibits slightly lower values than the ones of $[\text{C}_4\text{mim}][\text{TCM}]$ IL. The effect of the anion in this property was more complex to evaluate due to the large number of different techniques and not stated impurities (*e.g.* water) which affect the experimental data. Nevertheless, the cyano- and $[\text{PF}_6]^-$ -based ILs show higher surface tensions within the same range. Lower surface tensions, surface enthalpies and entropies are observed for $[\text{C}_n\text{mim}][\text{TF}_2\text{N}]$ ILs. In general, the surface enthalpies decrease with increasing alkyl chain length of the cation, while the surface entropy does not show a clear

dependency on the alkyl chain length. As expected the electrical conductivities decreases with increasing alkyl chain length. The data are described using VFT equation. The [TCM][−]-based ILs belong to the group of glass forming systems. The molar conductivities are calculated considering the densities and electrical conductivities. [TCM][−] ILs show ionicity that could be classified as that of good ionic liquids.

The experimental self-diffusion coefficients of the cations are in good agreement with the molecular simulations predictions, in which a decrease of the self-diffusivity of the cations with increasing alkyl chain length of the cation is observed. This trend is in agreement with the increase of the viscosity, displaying the effect of ion interaction and size on the mobility in the bulk liquid. From the molecular simulation predictions, it is possible to highlight the effect of increasing alkyl chain length on the self-diffusion of the [TCM][−] anion. As the alkyl chain length of the imidazolium cation becomes longer, the anion becomes more mobile than the cation. The self-diffusion coefficients of the [C₂mim]⁺ cation in [C₂mim][TCM] is higher than in [C₂mim][TCB], being related with the smaller size of the [TCM][−] anion and weaker intermolecular interactions. In general, the thermodynamic, structural and transport properties calculated using molecular simulation are in good agreement with the experimental data. This work is a complete contribution to the better understanding of the interesting properties of [C_nmim][TCM] (*n* = 2, 4 and 6–8) ILs that are currently identified as very promising candidates for use in a number of state-of-the art processes and applications.

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