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Influence of the alkyl side chain length on the thermophysical properties of chiral ionic liquids with a (1R,2S,5R)-(-)-menthol substituent and data analysis by means of mathematical gnostics

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Abstract

A comprehensive physico-chemical characterization of the chiral ionic liquids of a 3-alkyl-1-[(1R,2S,5R)-(-)-menthoxymethyl]imidazolium bis(trifluoromethylsulfonyl)imides homologous series with a linear alkyl substituent ranging from the methyl up to the dodecyl group was carried out experimentally to investigate the way in which the measured thermophysical properties were influenced by the alkyl chain length on the cation. Refractive index, density, speed of sound, and isobaric heat capacity were measured as a function of temperature at atmospheric pressure and analyzed by methods based on mathematical gnostics. A robust linear regression along a gnostic influence function was used to optimize parameters of the relationships used in this work and to estimate the changing nanosegregation in the studied ionic liquid series by finding the Critical Alkyl Length Size (CALS) from heat capacity data. In addition, we propose the use of the marginal analysis to assess the quality of the measured data as an alternative to the estimate of the measurement uncertainty.

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1. Introduction

In spite of the ever-increasing number of papers on ionic liquids (ILs), this class of compounds still hasn't used up its potential in terms of their possible applications. Not least importantly, establishing reliable relationships between their properties and structure will facilitate the utilization of ionic liquids and the design of new structures task-specific structures. Indeed, the number of possible combinations of different cations and anions is very large a rough estimate giving as many as 10¹⁸ ILs to be synthesizable. With a good knowledge of their structure-property relationships, their thermophysical characteristics such as the volumetric, transport, and thermal properties could thus be fitted to the

advantage of a particular application [1].

To contribute to a better understanding of the structure-property relationships of ionic liquids, a homologous series of ionic liquids with a chiral (1R, 2S, 5R)-(–)-menthol substituent and a bis(trifluoromethylsulfonyl)imide anion is dis-

- ¹⁵ cussed. A series of 3-alkyl-1-[(1R,2S,5R)-(-)-menthoxymethyl]imidazolium bis(trifluoromethylsulfonyl)imides was therefore studied in this work. Previously, the syntheses and basic physico-chemical characterization of the considered salts were described by our group [2, 3]. The presence of an optically active alcohol substituent in the cationic part causes these compounds to belong to the
- ²⁰ group of the chiral ionic liquids (CILs). We have noticed that the discussed optically active bis(trifluoromethylsulfonyl)imides series of salts might be applied in various fields of chemistry, among others in organic catalysis [4] or in stabilization and activation of laccase [5]. Furthermore, they have been proved to be effective antielectrostatic agents [2]. In a context of studies by other groups,
- ²⁵ Vasiloiu *et al.* [6] have for instance studied chiral ionic liquids that can be used as chiral selectors, chiral recognition being very difficult to predict.

Even though numerous papers address the influence of the linear alkyl sidechain length on the cation on the thermophysical and thermodynamic properties of ionic liquids, *e.g.* [7–15] to cite but a few, the relationships between those ³⁰ properties and the IL structure is far from established. Indeed, the interaction between the alkyl side chain and its cation and between the entire cation and the anion of the ionic liquid is very sensitive to even very small changes in structure. The influence of the alkyl chain length may often seem straightforward, however, nanostructure rearrangement was found to differ as a function of the alkyl

- chain length in homologous series based on the 1-alkyl-3-methylimidazolium cation. In a possibly first studies on the subject, Canongia-Lopes and Pádua [16] have explored nanostructure in 1-alkyl-3-methylimidazolium hexafluorophosphate ionic liquids by means of molecular simulation, showing nanosegregated polar and non-polar domains occurred, changing from disperse microphases
- ⁴⁰ for shorter chain lengths (C2) to continuous ones in ionic liquids with long alkyl substituents (C12). Later, Rocha *et al.* [17] used very precise measurements of vaporization enthalpies in a series of 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imides to determine a shift in the slope of the dependence of the vaporization enthalpy on the number of carbons in the alkyl
- ⁴⁵ chain on the cation, pointing towards that starting with hexyl-substituted ionic liquids nanostructuring changed its nature due to different coiling of the alkyl substituent. They state that this phenomenon was due to percolation effects and a pronounced decrease of the relative cation–anion interaction energy towards an almost constant value for alkyl substituents longer than hexyl, a finding they
- ⁵⁰ were able to confirm in several subsequent papers [8, 10, 18]. In the same homologous series, Garaga *et al.* [19] have used the NMR and vibrational spectra to show the displacement of the bis(trifluoromethylsulfonyl)imide anion for the methyl- to hexyl-substituted ionic liquids with a concomitant increase of the *trans* conformers and no further significant displacement for ionic liquids with
- ⁵⁵ alkyl chains longer than C6.

In this work a comprehensive physico-chemical experimental characterization of the chiral ionic liquids of the 3-alkyl-1-[(1R,2S,5R)-(-)-menthoxymethyl]imida-

zolium bis(trifluoromethylsulfonyl)imide series with alkyl ranging from the methyl up to the dodecyl substituent is carried out for two main reasons. In spite of

- the promising application potential of the entire series, such a study hasn't been carried out yet. The measured data not only prove useful in the design and optimization of a possible process in which the present ionic liquids will be used, but also contribute to the growing knowledgebase of the physico-chemical properties of pure ionic liquids and set them in context of previous studies by
- this group and other authors. The properties selected for study in this work, density, speed of sound, and heat capacity are linked through relationships following from the First and the Second Law of Thermodynamics and allow for a deriving of further material properties. Furthermore, density and heat capacity are related by the cohesive energy density, providing an insight into the influ-
- ⁷⁰ ence of the microstructure of the studied compounds on their bulk properties. As a consequence, specific heat capacity per unit volume calculated from the experimental molar heat capacity and liquid density may enable us to investigate possible structure rearrangement in the studied compounds, as their structure changes with the changing alkyl chain length on the cation [18].
- ⁷⁵ More importantly though, methods based on mathematical gnostics [20] were used in this work to process the measured data and to assess their quality. Mathematical gnostics not only enabled us to evaluate the repeatability of the measurements for the properties studied in this work, but mainly proved to be a valuable tool in assessing the structure-property relationships for the experi-
- ⁸⁰ mentally measured heat capacity in the studied series *via* the implementation of a robust linear regression along a gnostic influence function.

2. Theoretical section

2.1. Data quality assessment using the marginal analysis

The quality of experimental data is usually assessed from the measurement ⁸⁵ uncertainty the value of which follows from unknown systematic, random, and other, unidentified, errors of measurement. According to the NIST guidelines, [21] the combined uncertainty or preferably the expanded uncertainty of the measurement should be calculated from the data using any valid statistical method. However, this requires an *a priori* knowledge or at least an approxi-

- ⁹⁰ mation of the error distribution function and a data sample large enough to be statistically significant. Mathematical gnostics (MG) [20, 22] on the other hand, provides us with a non-statistical approach towards the uncertainty treatment without the need for an *a priori* assumption of the distribution of errors. The underlying theory was derived considering the uncertainty of every single mea-
- ⁹⁵ surement, the properties of a data sample are then evaluated by aggregation of properties of each measurement. Small data samples can thus be analyzed and a sound estimate of the experimental uncertainty obtained. The theory offers several tools each of which is suitable for a different application. For the purpose of this work we make use of the marginal analysis which is based on
- ¹⁰⁰ the properties of the estimating local distribution function (*ELDF*), namely on its natural robustness with respect to outliers. The mode of the *ELDF*'s density (Z_0) , *i.e.* the location of the density's maximum, is the most probable value of the data sample and is considered as an estimate of the true value of the measured quantity. The uncertainty is assessed by an estimation of the tolerance ¹⁰⁵ interval (Z_{0U} , Z_{0L}), and the interval of typical data (Z_{U} , Z_{L}) [20].

The intervals reflect the sensitivity of the ELDF's mode location to a single added data value. No matter how outlying the added value is the position of the mode cannot be shifted outside the tolerance interval (Z_{0U}, Z_{0L}) . Depending on the kind of analyzed data the tolerance interval represents either repeatability or reproducibility. The sensitivity of the mode location to the additional datum belonging to the interval of typical data (Z_U, Z_L) behaves typically, the dependence is increasing. If the additional datum falls outside this interval, the dependence becomes decreasing owing to the natural robustness of the *ELDF*. The interval of typical data thus delimits the range where a measured value can be expected. Values outside the interval of typical data are suspicious.

The symmetricity or asymmetricity of the estimating local distribution function, which can also be seen from the symmetricity or asymmetricity of the tolerance interval and the interval of typical data, provides us with an additional information on the character of experimental errors. The symmetric shape shows

that probability of positive and negative deviations is equal similarly as *e.g.* in the case of the Gaussian distribution. Asymmetric distribution is frequently found if the measured value is close to a physical limit of the quantity, typical example being data on trace analysis.

If the tolerance interval is symmetric or only slightly asymmetric, the uncertainty of the measurement for each datapoint can be expressed in a simpler form as:

$$Z = Z_0 \pm (Z_{0U} - Z_{0L})/2 \tag{1}$$

The overall measurement repeatability can then be estimated as the median of the uncertainties of the individual modes.

As already mentioned, this approach to uncertainty assessment does not require knowledge of distribution of experimental errors and is robust and reliable even if outliers are present in the data sample. The method suggested by the NIST guidlines [21] is based upon estimation of a variance of an *a priori* known distribution. If the data sample is small, we cannot verify the statistical distribution of errors and the relative error of estimated variance is high, often as

¹³⁵ much as 40%. Data with improperly assignd uncertainty based on statistical analysis do exist in the literature. One such case was mentioned in [23] and later in [22] where an analysis of reliability of estimation of a tolerance interval and an interval of typical data from real experimental data is presented.

2.2. Robust optimization along a gnostic influence function

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We have already shown in our previous work the importance of a reliable optimization algorithm in nonlinear regression tasks and how these can be carried out by means of robust regression along a gnostic influence function [24]. The regression along an influence function is not *per se* a concept derived in mathematical gnostics, it is indeed a statistical notion derived under an assumption that a limited number of measured values are subject to gross errors

with known non-Gaussian distribution [25]. However, such an assumption on the distribution of the gross errors can rarely be verified. Gnostic methods are based on more general assumptions of taking into account the uncertainty of the individual data points where the distribution function is also estimated during

- data analysis. Therefore, even though in this work the experimental data can be described by simple equations the parameters of which can be estimated by linear regression, the robust linear regression along the gnostic influence function based on mathematical gnostics was applied [20, 26]. For instance, if an outlier is identified, the regression algorithm assigns them with a lower weight.
- ¹⁵⁵ The optimized parameters can thus be considered as more reliable than the ones obtained from the statistical regression methods. On the other hand, when no outliers are present, the optimization becomes identical with the ordinary leastsquares method. In addition, the marginal analysis described in Section 2.1.1 enabled us to choose the appropriate empirical equation where there are no rec-
- ommended or thermodynamically justified relationships, e.g. in the description of the heat capacity data or to describe the dependencies of the measured properties on the number of carbon atoms in the alkyl substituent on the cation. Indeed, the marginal analysis of the regression residua provides us with the information of the residua dataset homogeneity or non-homogeneity. In the latter
- ¹⁶⁵ case the relationship may be considered as unsuitable for the given regression.

3. Experimental section

3.1. Chemicals used

(1R,2S,5R)-(-)-Menthol (99%), 1-methylimidazole (99%), 1-butylimidazole (98%), bromoethane (≥99%), 1-bromopropane (99%), 1-bromopentane (98%),
1-bromohexane (98%), 1-bromoheptane (99%), 1-bromooctane (99%), 1-bromononane (98%), 1-bromodecane (98%), 1-bromoundecane (98%), 1-bromododecane (97%), paraformaldehyde (powder, 95%), imidazole (≥99%), sodium (cubes, contains mineral oil, 99.9% trace metals basis) were purchased from Sigma-Aldrich, whereas lithium bis(trifluoromethylsulfonyl)imide (99%) was provided

¹⁷⁵ by IoLiTec. For the NMR analysis, the deuterated chloroform (CDCl₃) purchased from Merck was used. All the solvents were purchased from the commercial suppliers: Sigma-Aldrich and Fluka and were dried before use.

The structure and purity of all of the synthesised substances were confirmed by spectral and elemental analysis, respectively. The ¹H NMR and ¹³C NMR spectra were recorded on a Bruker DRX with tetramethylsilane as standard (at 600 and 151 MHz, respectively). Elemental analyses were carried out using VARIO EL-III.

The syntheses of 3-alkyl-1-[(1R,2S,5R)-(–)-menthoxymethyl]imidazolium bis(trifluoromethylsulfonyl)imides, abbreviation: [C_n-Im-CH₂OMen][Tf₂N],

- where n = 1 to 12, presented in this study were described in our previous publication [2]. For the sake of brevity the bis(trifluoromethylsulfonyl)imide anion will be referred to in this text as bistriflate. Elemental analysis was performed for all obtained salts and has been presented in the results section. All reagents were dried and purified before use by usual procedures, all substrates
- ¹⁹⁰ were freshly distilled before use [2]. Chloromethyl (1R,2S,5R)-(-)-menthyl ether was prepared by passing HCl through a mixture of (1R,2S,5R)-(-)-menthol and paraformaldehyde. 1-alkylimidazole were synthesized following the method by Pernak *et al.* [2]. Briefly, for quaternization chloromethyl (1R,2S,5R)-(-)-menthyl ether was slowly added to a solution of proper 1-alkyl-imidazole in dry hexane
- ¹⁹⁵ and vigorously stirred (from 60 min to 120 min) at room temperature. Then, the phases were separated and the product was washed with dry hexane. The volatile materials were removed under reduced pressure at 60 °C overnight. Obtained chlorides (200 mmol) were dissolved in water and saturated aqueous solution of lithium bis(trifluoromethylsulfonyl)imide (220 mmol) was added. The
- ²⁰⁰ metathesis reaction was stirred at room temperature for 24 h. Then, the crude product was separated and washed with distilled water three times. Respectively, each of the obtained ionic liquids was dissolved in acetone and stirred for 30 min to precipitate any residues of the halide salt, which was filtrated off (0.2 m filter). The filtrate was placed in the fridge (approx. -5 °C) for one night in
- $_{205}$ order to complete precipitation of the halide salt. In the case of precipitation

of inorganic salt, another filtration was carried out and the resulting filtrate was evaporated. This work-up was repeated until no more LiCl precipitate was observed (detected using $AgNO_3$) [27]. Elemental analysis was performed for all obtained salts and has been presented in the results section.

- ²¹⁰ 1-butanol anhydrous (purity 99.8%, Sigma-Aldrich) was used as received without any additional purification as a calorimetric standard. Throughout the experiments the amount of water in 1-butanol was checked by means of the Karl-Fischer titration and kept lower than 0.075 wt.%. Hydranal Titrant Composite 2 (titer 1.6–2.4 mg/ml) and Hydranal Methanol Dry (≥0.01 % water) used in
- the Karl-Fischer titrations were purchased from Sigma-Aldrich and used as received. 1-hexyl-3-methylimidazolium bis(trifluoro-methylsulfonyl)imide (abbr. [hmim][Tf₂N]) with a declared purity of 98% was purchased from IoLiTec to be used to validate the density, speed of sound, refractive index, and isobaric molar heat capacity measurements using the experimental protocol described herein.
 [hmim][Tf₂N] was decolorized before the experiments using the procedure described in the Electronic Supporting Information.

To further check the purity of the studied chiral ionic liquids and [hmim][Tf₂N], ion chromatography analysis both for cations (Li⁺, Na⁺, NH₄⁺, K⁺, Ca²⁺, and Mg²⁺) and anions (F⁻, Cl⁻, Br⁻, SO₄²⁻, NO₃⁻, H₂PO₄⁻) was carried out in parallel using a Dionex 5000 system. An IonPac AS11-HC 2 x 250 mm column was used for anions using hydroxide eluent, IonPac CS18 2 x 250 mm for cations using methane sulfonic acid solution as an eluent. Both anion and cation setup were equipped with electrochemical suppressors. External calibration was done using NIST traceable calibration solutions. The relative uncertainty of the ion

- ²³⁰ concentration determination was of 20% and the detection limit 0.001 ppm. Of the most important impurities that influence the properties of ionic liquids, chloride contents were found to be lower than 9.3 ppm for all the studied ionic liquids, whereas lithium contents were always lower than 0.1 ppm or below the detection limit of the device (see Table 2). IoLiTec states the level of the chloride
- anion in $[hmim][Tf_2N]$ to be lower than 100 ppm; it is evident from the present data that the real content of the impurities is much lower. The amounts of other

ionic impurities were found to be similarly low in the studied ionic liquids and are listed in Table SI-1. The overall purity of the ionic liquids studied in this work is then summarized in Table 1.

Table 1: Ionic liquids studied in the	his work			
Ionic Liquid	Source	Purification method	Final mass	Analysis
	CAS number		fraction purity	method
$[C_1-Im-CH_2OMen][Tf_2N]$	synthesis	(i) extraction ILs with water	0.99960	Karl-Fischer titration
		(ii) dissolving ILs in acetone		IC analysis
		(iii) drying <i>in vacuo</i>		
$[C_2-Im-CH_2OMen][Tf_2N]$	synthesis	(i) extraction ILs with water	0.99980	Karl-Fischer titration
		(ii) dissolving ILs in acetone		IC analysis
		(iii) drying <i>in vacuo</i>		
$[C_3-Im-CH_2OMen][Tf_2N]$	synthesis	(i) extraction ILs with water	0.99975	Karl-Fischer titration;
		(ii) dissolving ILs in acetone		IC analysis
		(iii) drying <i>in vacuo</i>		
$[C_4-Im-CH_2OMen][Tf_2N]$	synthesis	(i) extraction ILs with water	0.99978	Karl-Fischer titration;
		(ii) dissolving ILs in acetone		IC analysis
		(iii) drying <i>in vacuo</i>		
$[C_5-Im-CH_2OMen][Tf_2N]$	synthesis	(i) extraction ILs with water	0.99959	Karl-Fischer titration;
		(ii) dissolving ILs in acetone		IC analysis
		(iii) drying <i>in vacuo</i>		
$[C_6-Im-CH_2OMen][Tf_2N]$	synthesis	(i) extraction ILs with water	0.99978	Karl-Fischer titration;

Table 1 Continued from pre	evious page			
Ionic Liquid	Source	Purification method	Final mass	Analysis
	CAS number		fraction purity	method
		(ii) dissolving ILs in acetone		IC analysis
		(iii) drying <i>in vacuo</i>		
$[\mathrm{C}_{7}\text{-}\mathrm{Im}\text{-}\mathrm{CH}_{2}\mathrm{OMen}][\mathrm{Tf}_{2}\mathrm{N}]$	synthesis	(i) extraction ILs with water	0.99978	Karl-Fischer titration
		(ii) dissolving ILs in acetone		IC analysis
		(iii) drying <i>in vacuo</i>		
$[C_8-Im-CH_2OMen][Tf_2N]$	synthesis	(i) extraction ILs with water	0.99982	Karl-Fischer titration
		(ii) dissolving ILs in acetone		IC analysis
		(iii) drying <i>in vacuo</i>		
$[C_9-Im-CH_2OMen][Tf_2N]$	synthesis	(i) extraction ILs with water	0.99925	Karl-Fischer titration;
		(ii) dissolving ILs in acetone		IC analysis
		(iii) drying <i>in vacuo</i>		
$[\rm C_{10}\text{-}Im\text{-}CH_2OMen][\rm Tf_2N]$	synthesis	(i) extraction ILs with water	0.99996	Karl-Fischer titration
		(ii) dissolving ILs in acetone		IC analysis
		(iii) drying <i>in vacuo</i>		
$[\mathrm{C}_{11}\text{-}\mathrm{Im}\text{-}\mathrm{CH}_2\mathrm{OMen}][\mathrm{Tf}_2\mathrm{N}]$	synthesis	(i) extraction ILs with water	0.99979	Karl-Fischer titration
		(ii) dissolving ILs in acetone		IC analysis

	-			
Ionic Liquid Sc	ource	Purification method	Final mass	Analysis
C	CAS number		fraction purity	method
		(iii) drying <i>in vacuo</i>		
$[\rm C_{12}\text{-}Im\text{-}CH_2OMen][\rm Tf_2N] syl$	ynthesis	(i) extraction ILs with water	0.99972	Karl-Fischer titration
		(ii) dissolving ILs in acetone		IC analysis
		(iii) drying <i>in vacuo</i>		
$[hmim][Tf_2N]$ Ic	oLiTec	(i)active carbon and	0.99964	Karl-Fischer titration;
3(82150-50-7	column chromatography (silica gel)		IC analysis
		(ii) drying <i>in vacuo</i>		

To minimize contact with air moisture, the studied ionic liquids were kept in Schlenk flasks in a dessicator between the individual experiments. The samples were then dried before every experiment, for at least 16 hours under vacuum (8-10 mbar) at approximately 60 °C. The water content in the samples was determined by means of the volumetric Karl-Fischer titration using a Schott

Instruments GmbH TitroLine KF Titrator and did not exceed 0.00073 mass fraction units. The water contents in the samples along with the refractive indices of the studied ionic liquids are summarized in Table 2.

Table 2: Molar mass M_r , water and ion impurities contents, and refractive index, n_D^{25} , at 298.15 K of the studied chiral ionic liquids.

Chiral ionic liquid	$M{}_{\rm r}$ / g·mol^{-1}	$\rm H_2O$ / wt\%	Cl^- / ppm	Li^+ / ppm	n_D^{25}
$[\mathrm{C_n\text{-}Im\text{-}CH_2OMen}][\mathrm{Tf_2N}]$					
$[C_1\text{-}Im\text{-}CH_2OMen][Tf_2N]$	531.53	0.036	5.356	0.004	1.4483
$[\mathrm{C_2\text{-}Im\text{-}CH_2OMen}][\mathrm{Tf_2N}]$	545.56	0.018	2.061	0.014	1.4476
$[\mathrm{C}_3\text{-}\mathrm{Im}\text{-}\mathrm{CH}_2\mathrm{OMen}][\mathrm{Tf}_2\mathrm{N}]$	559.59	0.023	2.658	n.a.	1.4484
$[\mathrm{C}_4\text{-}\mathrm{Im}\text{-}\mathrm{CH}_2\mathrm{OMen}][\mathrm{Tf}_2\mathrm{N}]$	573.61	0.021	1.109	n.a.	1.4487
$[\mathrm{C}_5\text{-}\mathrm{Im}\text{-}\mathrm{CH}_2\mathrm{OMen}][\mathrm{Tf}_2\mathrm{N}]$	587.64	0.039	3.260	n.a.	1.4492
$[\mathrm{C}_{6}\text{-}\mathrm{Im}\text{-}\mathrm{CH}_{2}\mathrm{OMen}][\mathrm{Tf}_{2}\mathrm{N}]$	601.67	0.017	7.798	n.a.	1.4503
$[\mathrm{C}_{7}\text{-}\mathrm{Im}\text{-}\mathrm{CH}_{2}\mathrm{OMen}][\mathrm{Tf}_{2}\mathrm{N}]$	615.69	0.019	4.787	n.a.	1.4499
$[\mathrm{C_8\text{-}Im\text{-}CH_2OMen}][\mathrm{Tf_2N}]$	629.72	0.010	4.230	n.a.	1.4502
$[\mathrm{C}_9\text{-}\mathrm{Im}\text{-}\mathrm{CH}_2\mathrm{OMen}][\mathrm{Tf}_2\mathrm{N}]$	643.75	0.073	2.354	n.a.	1.4507
$[C_{10}\text{-}Im\text{-}CH_2OMen][Tf_2N]$	657.77	0.000	5.598	0.020	1.4508
$[C_{11}\text{-}Im\text{-}CH_2OMen][Tf_2N]$	671.80	0.020	1.968	0.045	1.4511
$[C_{12}\text{-}Im\text{-}CH_2OMen][Tf_2N]$	685.83	0.024	9.306	0.075	1.4518

 $U(w_{H_{2}O})=0.00001$ weight fraction units, $U_r(w_{ions}) = 20\%$, $U(n_D^{25})=0.00005$ refractive index units, U(T)=0.1 K, U(p)=0.02 MPa)

250 3.2. Experimental methods

All the experimental measurements were validated by measuring the thermophysical properties studied in this work for 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, analyzing the measured values by the marginal analysis described in Section 2.2.1 and comparing them with literature values (see Section 3.3).

3.2.1. Refractive index

The refractive index at 298.15 K at 0.1 MPa, n_D^{25} for the studied ionic liquids was measured by means of an AR Abbe refractometer 2 (A. Krüss Optronic GmbH) with an uncertainty of 0.0003 n_D units stated by the manufacturer. Before each measurement the refractive index of pure distilled water was measured and compared with its literature value ($n_D^{25}=1.3325$). [28]

3.2.2. Density and speed of sound

The density and the speed of sound as a function of temperature at 0.1 MPa were measured by means of an Anton Paar DSA5000 Density and Sound ²⁶⁵ Velocity Analyzer within the temperature range from (288.15 to 343.15) K. The speed of sound analyzer working frequence is of 3MHz. The apparatus was calibrated using degassed redistilled water (ρ =(0.997043±0.00001) g·cm⁻³ at T= 298.15 K) [29] and a high-density standard tetrachloroethylene supplied by H&D Fitzgerald Ltd. (ρ =(1.61420±0.00001) g·cm⁻³ at T=298.15 K).

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3.2.3. Isobaric heat capacity

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The isobaric heat capacity as a function of temperature at 0.1 MPa was measured by means of the differential scanning calorimetry. A Setaram μ DSC 3 Evo microcalorimeter based on the Tian-Calvet principle using batch cells was used. The continuous method with the heating rate of 0.3 K·min⁻¹ was used in this work, the initial and final temperatures of the scans being held constant for

²⁸⁰ 40 min in the same way as in [30]. The calibration data of 1-butanol that was used as the calibration standard were taken from the monograph by Zábranský

The uncertainty of the device stated by the manufacturer is of 0.00001 g·cm⁻³ for the density and of 0.1 m·s⁻¹ for the speed of sound. The apparatus is kept at the experimental temperature within ± 0.001 K by means of a built-in solid state thermostat.

et al. [31]. The heat capacity was then calculated by means of the Calisto software.

The standard and samples of pure ionic liquids, respectively, were prepared into the measuring cell by weighing using a SCALTEC SBC 21 balance with an accuracy of $\pm 1.10^{-5}$ g.

3.3. Validation of the density, speed of sound and heat capacity measurements

Due to the small amount of samples of the chiral ionic liquids available in this work, repeated measurements of the studied properties could not be carried out. To make sure that the present data were measured with adequate accuracy, density, speed of sound, refractive index, and isobaric molar heat capacity were measured using the experimental protocols described in Sections 3.2.1 to 3.2.3 for 1-hexyl-3-methylimidazolium bistriflate. The ionic liquid [hmim][Tf₂N] was selected as a benchmark ionic liquid for the IUPAC Project #2002-005-1-100

- (Thermodynamics of ionic liquids, ionic liquid mixtures, and the development of standardized systems), [32] the literature data on its thermophysical properties following from this project [33–42] may thus be considered as reliable. In addition, it is an imidazolium-based ionic liquid with a bistriflate anion, its chemical character is therefore similar to the ionic liquids studied in this work, being both prone to water uptake from air moisture as well as showing low solubility
- in water due to the hydrophilic character of the bistriflate anion.

Each measurement has been repeated at least five times and the data were analyzed by means of the marginal analysis described in Section 2.1. The measured refractive index, density, and speed of sound data are listed along with the estimated repeatability for the individual temperatures Tables SI-2 to SI-5 of the Electronic Supporting Information (ESI). The data are also compared with selected literature data in Tables SI-2 to SI-5 and Figure SI-4 of the ESI.

Table 3 then lists the repeatability of the measurements found by the marginal analysis as the median value of the individual datapoints uncertainty, the de-

vice precision stated by the manufacturers of the devices used in this work, and the reproducibility of the measurements found by the marginal analysis of our data together with literature values that followed from the IUPAC Project #2002-005-1-100 density [32-37], speed of sound [33], and isobaric molar heat capacity [38-42]. Data for the refractive index were not measured in the above-

- mentioned project, the data by Tariq et al. were therefore used [43]. As the 315 literature data were not all measured at the same temperatures as the present data, the comparison was made at a single temperature, *i.e.* at 298.15 K. The comparison of the individual values in Table 3 shows that the repeatability of the measurements found in this work is in good agreement with the uncertainty
- stated by the manufacturers of the devices used in this work. The overall un-320 certainty of the measurements can be estimated as where R is the measurement reproducibility, obtained in this work from the marginal analysis of our data together with the literature values, and N is the uncertainty following from the influence of the impurities in the studied ionic liquids. As the impurity levels
- found by the elemental analysis, ion chromatography, and Karl-Fischer titration 325 for the studied chiral ionic liquids and $[hmim][Tf_2N]$ are insignificantly low and sometimes even below the detection limit (especially for chloride and lithium ions, that are known to significantly influence the thermophysical properties of ionic liquids), the uncertainty following from the presence of impurities could be neglected and the overall measurement uncertainty was estimated as equivalent 330

to the repeatability found by the marginal analysis.

To compare the density, speed of sound, and isobaric molar heat capacity measured for $[hmim][Tf_2N]$ in this work with the data published within the IU-PAC Project #2002-005-1-100 and some more recent papers not related [44-46], a robust regression along a gnostic influence function described in Section 2.2 335 using equations used to describe the studied properties as a function of temperature was carried out for our data and literature values following from the IUPAC project. First all data, *i.e.* our data along with the literature values, were regressed. This regression was compared with that of literature data only and our data only, respectively, in Tables SI-6 to SI-8. Then, using the regression param-340 eters obtained from both our and literature data, the studied properties were

calculated to obtain deviations of the calculated data from the experimental

ones. These deviations are shown in Figures SI-1 to SI-3. From the regression parameters and the calculated deviations it appears that our data are in overall

- $_{345}$ good agreement with literature values. Indeed, the deviations calculated for the density data presented in this work are for all the three properties comparable with those obtained from the literature values. For instance, the isobaric molar heat capacity has been reported on in several works for [hmim][Tf₂N] in which different calorimetric methods over a wide range of temperatures were used.
- Furthermore, the robust regression along the gnostic influence function determines the weights of the individual datapoints *a posteriori*. From the regression of literature data along with those measured in this work it was evident that our data were assigned weights close to unity. This indicates that our data were not detected as outliers of the entire analyzed dataset. The comparison of our
- data with the literature is shown in Figure SI-3 and Figure SI-4. It appears that our data are in good agreement with those by Blokhin *et al.* [39] and Shimizu *et al.* [40], both obtained using adiabatic calorimetry with a state uncertainty of 2.5 J·K⁻¹·mol⁻¹ and 0.8 J·K⁻¹·mol⁻¹, respectively. Other data found in the literature [41, 42, 47, 48] show a larger scatter and deviation from the
- ³⁶⁰ present data, however, our data mostly fit into their uncertainty intervals of 11 J·K⁻¹·mol⁻¹ for Archer [41], 35 J·K⁻¹·mol⁻¹ for Diedrichs and Gmehling [42], and 22 J·K⁻¹·mol⁻¹ for Huges *et al.* [48]. It appears that the data measured in this work are of comparable if not better uncertainty than those obtained by these other authors.

Table 3: Data quality evaluation for the repeated measurements and the comparison with literature values of the refractive index at 298.15 K, and density and speed of sound as a function of temperature for $[hmim][Tf_2N]$

Measured property	Device precision ^a	$\operatorname{Repeatability}^{\mathrm{b}}$	Reproducibility ^c
Refractive index	$0.0003 n_{\rm D}$ units	$0.0001 n_{\rm D}$ units	$0.00005 n_{\rm D}$ units
Density	$1 \cdot 10^{-5} \mathrm{g \cdot cm^{-3}}$	$1 \cdot 10^{-5} \mathrm{g \cdot cm^{-3}}$	$0.00015 \text{ g} \cdot \text{cm}^{-3}$
Speed of sound	$0.1 \text{ m} \cdot \text{s}^{-1}$	$0.04~{\rm m}{\cdot}{\rm s}^{-1}$	${<}0.1~{\rm m}{\cdot}{\rm s}^{-1}$
Molar heat capacity	n/a	$0.17~\mathrm{J}{\cdot}\mathrm{K}^{-1}{\cdot}\mathrm{mol}^{-1}$	$1.1 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$

³⁶⁵ ^astated by the manufacturer

^bfound from the marginal analysis

^cfound from the marginal analysis from our and literature data [32–43]

Validating the use of 1-butanol as a reference liquid in heat capacity measure-³⁷⁰ ments was carried out in a previous work [30]. By measuring the heat capacity of water using the 1-butanol standard it was shown that heat capacity could be measured with good accuracy, the deviation from the recommended data not exceeding 0.25%. Thus 1-butanol can be considered as a suitable reference material despite its relatively high hygroscopicity. This was further confirmed ³⁷⁵ by validating the measurements against the literature values of heat capacity of [hmim][Tf₂N]. To make sure that the standard did not absorb an excessive amount of water during the calibration run, a Karl-Fischer titration was performed before and after each calibration, the amount of water not exceeding 0.0007 mass fraction units in any of the experiments.

380 4. Results and Discussion

4.1. Synthesis

The homologous series of chiral ionic liquids with a (1R,2S,5R)-(-)-menthol substituent and bistriflate anion were prepared. The synthesized salts were obtained in very good yields, higher than 96% in each case. All details are 385 given in Table 4. All ionic liquids discussed in here are hydrophobic, colourless liquid and are stable in water solution.

Schema 1 shows the general structure of the synthesized 3-alkyl-1-[(1R,2S,5R)-(-)-menthoxymethyl] imidazolium bis(trifluoromethylsulfonyl)imides. The ionic liquids were characterized by ¹H NMR and ¹³C NMR (see Electronic Support-

³⁹⁰ ing Information File 2). Elemental analysis was performed for all discussed salts and the details are given in Table 4.

Schema 1. Structure of the synthesized 3-alkyl-1-[(1R,2S,5R)-(-)-menthoxymethyl]imidazolium bis(trifluoromethylsulfonyl)imides (R=CH₃ to C₁₂H₂₅)

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CILs	Abbreviation	R	Yield [%]	$\operatorname{Empirical}$	Elementary analysis	Elementary analysis
	$[C_n-ImCH_2OMen][Tf_2N]$			formula	calculation [%]	found [%]
1	$[C_1-Im-CH_2OMen][Tf_2N]$	CH_3	99.5	${\rm C}_{17}{\rm H}_{27}{\rm F}_6{\rm N}_3{\rm O}_5{\rm S}_2$	C 38.40, H 5.13, N 7.91	C 38.49, H 5.27, N 7.82
7	$[C_2-Im-CH_2OMen][Tf_2N]$	C_2H_5	99.5	$\rm C_{18}H_{29}F_6N_3O_5S_2$	C 39.61, H 5.37, N 7.70	C 39.48, H 5.49, N 7.76
e	$[C_3-Im-CH_2OMen][Tf_2N]$	$\mathrm{C}_3\mathrm{H}_7$	99.0	$\rm C_{19}H_{31}F_6N_3O_5S_2$	C 40.77, H 5.59, N 7.51	C 40.89, H 5.69, N 7.40
4	$[C_4-Im-CH_2OMen][Tf_2N]$	C_4H_9	99.5	$C_{20}H_{33}F_6N_3O_5S_2$	C 41.86, H 5.81, N 7.32	C 41.77, H 5.90, N 7.39
ъ	$[C_5-Im-CH_2OMen][Tf_2N]$	C_5H_{11}	98.0	$\rm C_{21}H_{35}F_6N_3O_5S_2$	C 42.91, H 6.01, N 7.15	C 42.83, H 6.15, N 7.20
9	$[C_6-Im-CH_2OMen][Tf_2N]$	$\mathrm{C_6H_{13}}$	98.5	$\rm C_{22}H_{37}F_6N_3O_5S_2$	C 43.90, H 6.21, N 6.98	C 43.96, H 6.29, N 6.88
7	$[C_7-Im-CH_2OMen][Tf_2N]$	$\rm C_7H_{15}$	97.5	$C_{23}H_{39}F_6N_3O_5S_2$	C 44.85, H 6.40, N 6.82	C 44.89, H 6.49, N 6.70
x	$[C_8-Im-CH_2OMen][Tf_2N]$	$\mathrm{C_8H_{17}}$	0.60	$\rm C_{24}H_{41}F_6N_3O_5S_2$	C 45.76, H 6.57, N 6.67	C 45.65, H 6.63, N 6.59
6	$[C_9-Im-CH_2OMen][Tf_2N]$	$\mathrm{C_9H_{19}}$	97.0	$\rm C_{25}H_{43}F_6N_3O_5S_2$	C 46.63, H 6.74, N 6.53	C 46.70, H 6.67, N 6.45
10	$[C_{10}-Im-CH_2OMen][Tf_2N]$	$\mathrm{C}_{10}\mathrm{H}_{21}$	98.5	$\rm C_{26}H_{45}F_6N_3O_5S_2$	C 47.46, H 6.91, N 6.39	C 47.30, H 6.99, N 6.43
11	$[\mathrm{C}_{11}\text{-}\mathrm{Im}\text{-}\mathrm{CH}_2\mathrm{OMen}][\mathrm{Tf}_2\mathrm{N}]$	$\mathrm{C}_{11}\mathrm{H}_{23}$	96.5	$\rm C_{27}H_{47}F_6N_3O_5S_2$	C 48.25, H 7.06, N 6.25	C 48.36, H 7.12, N 6.19
12	$[C_{12}-Im-CH_2OMen][Tf_2N]$	$\mathrm{C_{12}H_{25}}$	97.5	$\rm C_{28}H_{49}F_6N_3O_5S_2$	C 49.02, H 7.21, N 6.13	C 48.95, H 7.33, N 6.18

³⁹⁵ 4.2. Measurement of thermophysical properties

4.2.1. Refractive index

Figure 1: Refractive index, n_D^{25} , at 298.15 K of the studied chiral ionic liquids [C_n-Im-CH₂OMen][Tf₂N] as a function of carbon atoms, n(C), in the alkyl chain on the cation. Black circles are experimental data.

Refractive indices measured at 298.15 K for the studied ionic liquids are summarized in Table 2 and plotted as a function of the number of carbons of the alkyl substituent in Figure 1. The data display a slight deviation from a regular increase. Since

- the refractive index is very sensitive to small changes in concentration, this deviation could be caused by minor impurities in the individual IL samples and/or slightly differing water contents. The deviation of the refractive index of the methyl-substituted ionic liquid $[C_1-Im-CH_2OMen][Tf_2N]$ might also be attributed to the different packing of this first member of the homologous series as for instance in the homologous series
- 405 of alkanes [49].

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4.2.2. Density and speed of sound

The experimental data on density and speed of sound as a function of temperature are listed in Tables SI-9 and SI-10 of the ESI, respectively. Density of the studied ionic liquids decreases with increasing temperature. The experimental density data were described with the linear equation

$$\rho = A + BT \tag{2}$$

Figure 2: Experimental density, ρ , at 298.15 K of the studied chiral ionic liquids [C_n-Im-CH₂OMen][Tf₂N] as a function of the number of carbons of the alkyl side chain length n(C). Black circles are experimental data, full line corresponds to the fit by Eq. 5.

Some authors seem to point to a controversy around the choice of a linear or quadratic dependence of the logarithm of density on temperature [50, 51]. However, the reasons for choosing one or another are purely empirical (assuming that the coefficient of the isobaric expansivity barely changes with temperature) or based on the goodness 415 of fit. In the case of the data presented in this work, the linear and quadratic fit for the logarithm of density as a function of temperature were both found to provide non-random patterns for the calculated residuals. However, the selected fit influences the value of the coefficient of isobaric expansivity defined as

$$\alpha_p = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right) \tag{3}$$

A differentiable function can be approximated by an expansion to a Taylor series. Considering the partial derivative of the density with respect to temperature at constant pressure as the first term of a Taylor series and that the coefficient of isobaric expansivity is almost independent of temperature, it increases only very slightly with temperature in the condensed phase, it becomes evident that a linear function should be sufficient to describe the temperature dependence of density.

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The parameters of Eq. 2 that are summarized in Table 5 were optimized using a robust linear regression algorithm along a gnostic influence function as described in section 2.1.2. For this and all the following regression functions used in this work, the Standard Estimation of Error, SEE, was calculated from the sum of squares of weighted regression residua as

$$SEE = \sum_{i=1}^{n} \left\{ w_i \left(y_i^{exp} - y_i^{calc} \right) \right\}^2 \tag{4}$$

where *n* is the number of datapoints, w_i is the robustifying weight of the point *i* obtained on the regression of data along a gnostic influence function and y_i^{exp} and y_i^{calc} are experimental and calculated values, respectively.

Density at 303.15 K of the studied chiral ionic liquids that have already been reported in previous work were compared with those found in this work. Differences ⁴³⁵ between the values reported herein and in Ref. [2] range between (0.1 and 30) kg·m⁻³ and may explained by two main aspects. In Ref. [2] a simple gravimetric method using a Mettler Toledo DA 110 M scale was used to measure the density of the studied

ionic liquids the uncertainty of which is significantly higher than that of the vibrating tube densitometry used in this work. Further contributing to the different values of
the measured density was the different purification protocol used in previous work; as compared with the procedure described in Section 3.1 the ionic liquids in Ref. [2] were only washed with distilled water. The density reported on was thus not only measured with lower uncertainty and as a function of temperature, but also using ionic liquids with higher purity.

Chiral ionic liquid	$A/ \mathrm{g \cdot cm^{-3}}$	$B \ 10^4 / \text{ g} \cdot \text{cm}^{-3} \cdot \text{K}^{-1}$	$SEE \ 10^7/ \ {\rm g} \cdot {\rm cm}^{-3}$
$[\mathrm{C_n\text{-}Im\text{-}CH_2OMen}][\mathrm{Tf_2N}]$			
$[C_1\text{-}Im\text{-}CH_2OMen][Tf_2N]$	1.5998	-8.9592	1.5
$[\mathrm{C_2\text{-}Im\text{-}CH_2OMen}][\mathrm{Tf_2N}]$	1.5746	-8.8238	1.8
$[\mathrm{C}_3\text{-}\mathrm{Im}\text{-}\mathrm{CH}_2\mathrm{OMen}][\mathrm{Tf}_2\mathrm{N}]$	1.5510	-8.7013	1.1
$[\mathrm{C}_4\text{-}\mathrm{Im}\text{-}\mathrm{CH}_2\mathrm{OMen}][\mathrm{Tf}_2\mathrm{N}]$	1.5296	-8.5662	0.9
$[\mathrm{C}_5\text{-}\mathrm{Im}\text{-}\mathrm{CH}_2\mathrm{OMen}][\mathrm{Tf}_2\mathrm{N}]$	1.5111	-8.4850	0.7
$[\mathrm{C}_{6}\text{-}\mathrm{Im}\text{-}\mathrm{CH}_{2}\mathrm{OMen}][\mathrm{Tf}_{2}\mathrm{N}]$	1.4871	-8.3716	0.6
$[\mathrm{C_7\text{-}Im\text{-}CH_2OMen}][\mathrm{Tf_2N}]$	1.4731	-8.2991	0.7
$[\mathrm{C_8\text{-}Im\text{-}CH_2OMen}][\mathrm{Tf_2N}]$	1.4622	-8.2233	0.5
$[\mathrm{C}_9\text{-}\mathrm{Im}\text{-}\mathrm{CH}_2\mathrm{OMen}][\mathrm{Tf}_2\mathrm{N}]$	1.4480	-8.1521	0.5
$[\mathrm{C}_{10}\text{-}\mathrm{Im}\text{-}\mathrm{CH}_2\mathrm{OMen}][\mathrm{Tf}_2\mathrm{N}]$	1.4363	-8.1174	0.5
$[C_{11}\text{-}Im\text{-}CH_2OMen][Tf_2N]$	1.4227	-8.0493	0.5
$[C_{12}\text{-}Im\text{-}CH_2OMen][Tf_2N]$	1.4108	-7.9754	0.3

Table 5: Parameters A and B of the linear relationship Eq. 2 used to describe density, ρ , of the chiral ionic liquids [C_n-Im-CH₂OMen][Tf₂N] as a function of temperature.

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Data listed in Table 6 and shown in Figure 2 then illustrate the influence of the alkyl chain length on the cation on the density and molar volume of the studied ionic liquids at 298.15 K. Not surprisingly, the molar volume shows an increasing function of the alkyl chain length, the density decreasing correspondingly. Indeed, due to steric hindrance, the longer alkyl side chain was found to contribute to a poorer packing, a

⁴⁵⁰ trend described not only for imidazolium-based ionic liquids by *e.g.* Rocha *et al.* [7, 8], but also in one of our previous work addressing a series of alkyl-triethylammoniumbased ionic liquids [9].

Chiral ionic liquid	$\rho/ \mathrm{g \cdot cm^{-3}}$	$V_m \ / \ \mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$
$[Cn\text{-}Im\text{-}CH_2OMen][Tf_2N]$		
$[C_1\text{-}Im\text{-}CH_2OMen][Tf_2N]$	1.33263	398.86
$[C_2\text{-}Im\text{-}CH_2OMen][Tf_2N]$	1.31157	415.96
$[C_3\text{-}Im\text{-}CH_2OMen][Tf_2N]$	1.29152	433.28
$[C_4\text{-Im-CH}_2OMen][Tf_2N]$	1.27421	450.17
$[\mathrm{C}_5\text{-}\mathrm{Im}\text{-}\mathrm{CH}_2\mathrm{OMen}][\mathrm{Tf}_2\mathrm{N}]$	1.25813	467.07
$[C_6\text{-Im-CH}_2OMen][Tf_2N]$	1.23746	486.20
$[\mathrm{C_7\text{-}Im\text{-}CH_2OMen}][\mathrm{Tf_2N}]$	1.22565	502.34
$[C_8\text{-Im-CH}_2OMen][Tf_2N]$	1.21701	517.43
$[C_9\text{-Im-CH}_2OMen][Tf_2N]$	1.20491	534.27
$[\mathrm{C}_{10}\text{-}\mathrm{Im}\text{-}\mathrm{CH}_2\mathrm{OMen}][\mathrm{Tf}_2\mathrm{N}]$	1.19429	550.76
$[\mathrm{C}_{11}\text{-}\mathrm{Im}\text{-}\mathrm{CH}_2\mathrm{OMen}][\mathrm{Tf}_2\mathrm{N}]$	1.18275	568.00
$[C_{12}\text{-}Im\text{-}CH_2OMen][Tf_2N]$	1.17306	584.65

Table 6: Experimental density, ρ , and molar volume, V_m , for the studied chiral ionic liquids [C_n-Im-CH₂OMen][Tf₂N] at 298.15 K.

 $U(\rho){=}0.00015~{\rm g}{\cdot}{\rm cm}^{-3}$, $U(T){=}0.01$ K, $U(p){=}0.02{\rm MPa}$

The dependence of the density on the alkyl chain length was correlated with a 455 cubic function that was found to optimally describe the data:

$$\rho = A + Bn(C) + Cn^{2}(C) + Dn^{3}(C)$$
(5)

Using the gnostic marginal analysis, residua of both a quadratic and cubic equation fit were analyzed showing that in the former, the regression residua were nonhomogeneous whereas for the latter they were found homogeneous. The parameters of the cubic equation fit are given in Table 7.

Table 7: Coefficients A, B, C, and D of the cubic relationship Eq. 5 used to describe density, ρ , at 298.15 K of the chiral ionic liquids [C_n-Im-CH₂OMen][Tf₂N] as a function of the number of carbons in the alkyl side chain on the cation.

$A/ \text{ g} \cdot \text{cm}^{-3}$	$B/ \mathrm{g \cdot cm^{-3}}$	$C/ \mathrm{g \cdot cm^{-3}}$	$D/ \mathrm{g \cdot cm^{-3}}$	$SEE \ 10^5/{ m g}\cdot{ m cm}^{-3}$
1.356	-0.02448	0.00112	-0.00003	4.9

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Similarly to density, speed of sound of the studied ionic liquids is a decreasing

function of temperature. In this work the dependence was found to be non-linear. Marczak [52] and Bilanyuk and Wong [53] proposed a simple fifth-order polynomial to model the temperature-dependence of the speed of sound in pure water. In this work, using a robust linear regression algorithm along a gnostic influence function (see

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section 2.4.) to the fourth-order polynomial was found to fit the data more precisely, with a lower *SEE* than a fit with a fifth-order polynomial. Table 8 lists the optimized parameters of Eq. 6 for the studied $[C_n-Im-CH_2OMen][Tf_2N]$ chiral ionic liquids

$$u = A + BT + CT^{2} + DT^{3} + ET^{4}$$
(6)

tion Eq. 6 used to describe the speed of sound, u , of the chiral ionic	
Table 8: Parameters A, B, C, D , and E of the fourth-order polynomial equ	liquids [C _n -Im-CH ₂ OMen][Tf ₂ N] as a function of temperature.

Chiral ionic liquid	$A 10^{-3}/$	B/	$C 10^2/$	$D 10^4/$	$E 10^7/$	$SEE/m \cdot s^{-1}$
$[C_n-ImCH_2OMen][Tf_2N]$	$\mathrm{m}{\cdot}\mathrm{s}^{-1}$	$m{\cdot}s^{-1}{\cdot}K^{-1}$	$\mathrm{m}{\cdot}\mathrm{s}^{-1}{\cdot}\mathrm{K}^{-2}$	$m{\cdot}s^{-1}{\cdot}K^{-3}$	$m{\cdot}s^{-1}{\cdot}K^{-4}$	
[C ₁ -ImCH ₂ OMen][Tf ₂ N]	8.37	-32.62	-7.65	5.85	-7.68	2.39
$[C_2-ImCH_2OMen][Tf_2N]$	4.40	0.76	-16.10	6.18	-6.87	0.59
$[C_3-ImCH_2OMen][Tf_2N]$	-0.90	77.78	-56.93	0.16	-0.15	0.82
$[C_4-ImCH_2OMen][Tf_2N]$	5.91	-11.98	-12.82	6.02	-7.12	0.62
$[C_5-ImCH_2OMen][Tf_2N]$	4.07	13.32	-25.62	8.86	-9.46	0.59
$[C_6-ImCH_2OMen][Tf_2N]$	5.57	-2.94	-19.03	7.69	-8.71	0.64
$[C_7-ImCH_2OMen][Tf_2N]$	-5.43	124.59	-74.31	18.30	-16.31	0.53
$[C_8-ImCH_2OMen][Tf_2N]$	7.05	-26.65	-5.59	4.42	-5.8	0.44
$[C_9-ImCH_2OMen][Tf_2N]$	3.22	18.96	-25.90	8.44	-8.77	0.45
$[\mathrm{C_{10}\text{-}ImCH_2OMen}][\mathrm{Tf_2N}]$	7.85	-46.21	7.98	0.71	-2.23	0.21
$[C_{11}-ImCH_2OMen][Tf_2N]$	2.58	28.85	-31.53	9.86	-10.10	0.11
$[C_{12}-ImCH_2OMen][Tf_2N]$	3.70	9.69	-19.90	6.84	-7.26	0.20

Figure 3 represents the speed of sound as a function of the alkyl chain length on the cation at 298.15 K. Similarly to the refractive index data, it appears that there is
no straightforward trend in this dependence, the first six members of the homologous series not corresponding to the increasing trend of the remaining ionic liquids with alkyl chain substituents longer than C3. Methyl- through pentyl-substituted ionic liquids show an alternation in the values of the speed of sound with odd-numbered members of the homologous series showing higher values than the even-numbered ones.

- ⁴⁷⁵ This trend was not observed in the measured density. It may, however, be said that a similar alternation is given for alkanes for their melting points in almost every organic chemistry textbook. Boese *et al.* [49] have shown this alternation in melting points and density of alkanes who used X-ray crystallography to explain this phenomenon by the different crystallization patterns. Considering ionic liquids as molten salts that unlike
- 480 molecular liquids do not have a completely random structure in the liquids phase, the difference in the odd-even alkyl chain packing could be a plausible explanation of the trend found in this work for the speed of sound of the studied ionic liquids

Figure 3: Speed of sound, u, at 298.15 K for the studied chiral ionic liquids [C_n-Im-CH₂OMen][Tf₂N] as a function of number of carbon atoms in alkyl chain n (C). Black circles are experimental data.

The coefficient of isobaric expansivity α_P calculated as a function of temperature using its definition (Eq. 3) and the linear fit of the density dependence on temperature (Eq. 2) is summarized in Table SI-10 and in Figure SI-5. It appears from the calculated values that it increases only insignificantly with temperature, in the range of 6.7 10⁻⁴ to $6.9 \, 10^{-4} \, \text{K}^{-1}$ for the studied temperature range. Figure 4 then shows that the coefficient of isobaric expansivity shows a rather irregular increase with the increasing alkyl chain length on the cation. Interestingly, such an irregular trend was also found by Rocha et al. [8] for α_P as well as for the standard molar Gibbs energy, and enthalpy and entropy of vaporization in series of asymmetric 1-alkyl-3-methylimidazolium bistriflate and symmetric 1,3-dialkylimidazolium bistriflate ionic liquids.

Figure 4: The coefficient of the isobaric expansivity α_P for the chiral ionic liquids [C_n-Im-CH₂OMen][Tf₂N] at 298.15 K as a function of the number of carbons in the alkyl substituent, n(C).

Using the speed of sound data, the isentropic compressibility was also calculated and is given in Table SI-12 and Figure SI-6 of the ESI

$$\kappa_S = 1/\left(\rho u^2\right) \tag{7}$$

495 4.2.3. Isobaric molar heat capacity

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The experimental isobaric molar heat capacity $C_{p,m}$ as a function of temperature is summarized for all the studied ionic liquids in Table SI-13 and represented in Figure SI-7 of the ESI. The heat capacity is an increasing function of temperature, usually best fitted with a function of a polynomial character [54]. In this work the robust linear regression along the gnostic influence function was used to find that the following function gives the best fit

$$C_{p,m} = A + BT + CT^2 + DT^3 \tag{8}$$

Table 9 then lists the coefficients of Eq. 8 for the studied $[C_n-Im-CH_2OMen][Tf_2N]$ chiral ionic liquids.

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Chiral ionic liquid	$A 10^2/$	B/	$C 10^2 /$	$D 10^5 /$	SEE /
$[C_n-Im-CH_2OMen][Tf_2N]$	$J{\cdot}K^{-1}{\cdot}mol^{-1}$	$J.K^{-2}.^{-1}$	$J{\cdot}K^{-3}{\cdot}mol^{-1}$	$J{\cdot}K^{-4}{\cdot}mol^{-1}$	$J \cdot K^{-1} \cdot mol^{-1}$
$[C_1-Im-CH_2OMen][Tf_2N]$	5.9640	6.3395	-1.8922	2.1624	0.14179
$[C_2-Im-CH_2OMen][Tf_2N]$	5.9326	6.2605	-1.7457	1.9023	0.47536
$[C_3-Im-CH_2OMen][Tf_2N]$	6.5423	6.8896	-2.0916	2.4402	0.50848
$[C_4-Im-CH_2OMen][Tf_2N]$	6.8816	7.2387	-2.2458	2.6667	0.61303
$[C_5-Im-CH_2OMen][Tf_2N]$	6.9235	7.3580	-2.2112	2.5603	0.34356
$[C_6-Im-CH_2OMen][Tf_2N]$	7.9528	8.3652	-2.7702	3.4375	1.0435
$[C_7-Im-CH_2OMen][Tf_2N]$	7.5926	7.9863	-2.4828	2.9630	0.76051
$[C_8-Im-CH_2OMen][Tf_2N]$	8.2841	8.7146	-2.8542	3.5183	1.2084
$[\mathrm{C_9-Im} ext{-}\mathrm{CH_2OMen}][\mathrm{Tf_2N}]$	7.3285	7.8486	-2.2197	2.4786	0.10154
$[\mathrm{C}_{10} ext{-}\mathrm{Im} ext{-}\mathrm{CH}_2\mathrm{OMen}][\mathrm{Tf}_2\mathrm{N}]$	7.8941	8.3071	-2.4644	2.8684	1.9705
$[C_{11}-Im-CH_2OMen][Tf_2N]$	8.5536	9.0214	-2.7880	3.3173	0.72757
$[C_{12}-Im-CH_2OMen][Tf_2N]$	7.6582	8.2498	-2.2195	2.3927	0.34792

 $U(C_{pm}) = 1.1$ J·K⁻¹·mol⁻¹, U(T) = 0.01 K, U(p) = 0.02 MPa

⁵⁰⁵ Using the molar heat capacity data and the calculated coefficient of isentropic compressibility and isobaric expansivity, the isothermal compressibility coefficient

$$\kappa_T = \kappa_S + \frac{\alpha_P T M}{\rho C_{p,m}} \tag{9}$$

and the isochoric molar heat capacity

$$C_{V,m} = C_{p,m} - \frac{\alpha_P T M}{\rho \kappa_T} \tag{10}$$

were calculated and are listed in Tables SI-12 and SI-14 of the ESI, respectively.

Table 10 and Figure 5 give the dependence of the isobaric molar heat capacity on the alkyl chain length at 298.15 K. Molar heat capacity data were fitted with a linear relation

$$C_{p,m}^{o} = A + Bn(C) \tag{11}$$

the parameters of which are given in Table 11 and show a contribution of the methylene group to the heat capacity of 30.86 J·K⁻¹·mol⁻¹. This value may be considered to be within reasonable agreement with the value of (32.1±0.3) J·K⁻¹·mol⁻¹ found by Paulechka [55] in his review of the ionic liquids heat capacity for the series of 1-alkyl-3-methylimidazolium bistriflates. However, Rocha *et al.* [18] showed both by analyzing heat capacity data and by molecular simulation that the nanosegregation in ionic liquids was different for 1-alkyl-3-methylimidazolium bistriflates with alkyls from methyl to hexyl than for those with alkyl substituents longer than hexyl, finding the so-called Critical Alkyl Length Size (CALS). This difference leads to a trend shift in several thermophysical properties, for instance the enthalpy of vaporization, viscosity,

- and heat capacity [17, 18], but also in surface tension [56]. As appears from Table 11, the *SEE* of the linear fit of Eq. 11 to the experimental heat capacity is significantly larger than the measurement uncertainty of the molar heat capacity measurements
- found in this work. This could mean that even though no apparent trend shift can be observed from the dependence of $C_{p,m}^{o}$ on the alkyl chain length shown in Figure 5, the data are not quite linear. Since the trend-shift is related to changes in cohesive energy/strength in the studied liquids, it is more apparent in specific heat capacity, C_{p}^{o} , and particularly in specific heat capacity per unit volume, C_{p}^{o}/V data [18]. These
- were therefore calculated in this work at 298.15 K from the experimental molar heat capacity and density and are summarized in Table 10.

Chiral ionic liquid	$C_{p,m}^o/$ J·K ⁻¹ ·mol ⁻¹	$C_p^o/ \mathrm{J}\cdot\mathrm{K}^{-1}\cdot\mathrm{g}^{-1}$	C_p^o/V / J·K ⁻¹ ·cm ⁻³
$[\mathrm{C_n\text{-}Im\text{-}CH_2OMen}][\mathrm{Tf_2N}]]$			
$[C_1\text{-}Im\text{-}CH_2OMen][Tf_2N]$	781.4	1.47	1.96
$[C_2\text{-Im-CH}_2\text{OMen}][Tf_2N]$	819.2	1.50	1.97
$[\mathrm{C}_3\text{-}\mathrm{Im}\text{-}\mathrm{CH}_2\mathrm{OMen}][\mathrm{Tf}_2\mathrm{N}]$	841.8	1.50	1.94
$[C_4\text{-}Im\text{-}CH_2OMen][Tf_2N]$	868.9	1.51	1.93
$[C_5\text{-}Im\text{-}CH_2OMen][Tf_2N]$	906.9	1.54	1.94
$[\mathrm{C}_{6}\text{-}\mathrm{Im}\text{-}\mathrm{CH}_{2}\mathrm{OMen}][\mathrm{Tf}_{2}\mathrm{N}]$	942.8	1.57	1.94
$[\mathrm{C_7\text{-}Im\text{-}CH_2OMen}][\mathrm{Tf_2N}]$	959.6	1.56	1.91
$[C_8\text{-}Im\text{-}CH_2OMen][Tf_2N]$	993.8	1.58	1.92
$[C_9\text{-}Im\text{-}CH_2OMen][Tf_2N]$	1024.0	1.59	1.92
$[C_{10}\text{-Im-CH}_2\text{OMen}][Tf_2N]$	1046.5	1.59	1.90
$[C_{11}\text{-}Im\text{-}CH_2OMen][Tf_2N]$	1090.7	1.62	1.92
$[C_{12}\text{-}Im\text{-}CH_2OMen][Tf_2N]$	1121.5	1.63	1.92

Table 10: Isobaric molar heat capacities, $C_{p,m}^{o}$, specific heat capacities C_{p}^{o} and specific heat capacities per volume C_{p}^{o}/V for studied ionic liquids at 298.15 K as a function of the number of carbon atoms in the alkyl group on the cation.

 $U(C_{pm})=1.1 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}, U(T)=0.01 \text{ K}, U(p)=0.02 \text{ MPa}$

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Figure 5: Molar isobaric heat capacities, $C_{p,m}^{o}$, at 298.15 K and 0.1 MPa for the studied [C_n-Im-CH₂OMen][Tf₂N] chiral ionic liquids as a function of the number of carbon atoms, n(C), in the alkyl group on the cation. Black circles are experimental data.

Table 11: Parameters A and B of the linear relationship Eq. 11 used to describe the isobaric molar heat capacity, $C_{p.m}$, of the chiral ionic liquids [C_n-Im-CH₂OMen][Tf₂N] as a function of the number of carbon atoms in the alkyl group on the cation.

A/ $J \cdot K^{-1} \cdot g^{-1}$	$\rm B/~J{\cdot}K^{-1}{\cdot}mol^{-1}$	$\rm SEE/~J{\cdot}K^{-1}{\cdot}mol^{-1}$
749.71	30.86	350.43

Figure 6 represents the dependence of C_p^o/V on the alkyl chain length calculated from the raw data of heat capacity and density. Even though a change in the slope of the dependence is apparent and a trend-shift may be expected at *approx*. n=6, the data are too scattered to enable us to carry out a reliable linear regression to estimate Figure 6: Isobaric heat capacity per unit volume, C_p^o/V , at 298.15 K for the studied [C_n-Im-CH₂OMen][Tf₂N] chiral ionic liquids as a function of the number of carbon atoms in the alkyl group on the cation, n(C). White circles are data calculated from raw density and isobaric specific heat capacity, black circles are data calculated from smoothed density and isobaric specific heat capacity, full lines are linear regression of the C_p^o/V data for the combination of CH₃ to C₄H₉ and C₉H₁₉ to C₁₂H₂₅ substituted ionic liquids.

whether the trend-shift at CALS found by Rocha *et al.* [18] in the homologous series of 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imides could also be found in this series. Therefore, Eq. 5 was used to calculate smoothed density data, whereas the specific heat capacity data were regressed with a linear equation (see Table 12 for the optimized parameters)

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substituted ILs), respectively:

$$C_p^o = A_{spec} + B_{spec} n(C) \tag{12}$$

 C_p/V were then calculated from the smoothed density and specific heat capacity data and is shown as a function of the alkyl chain length in Table 13 and Figure 6. To find CALS, the datapoints were divided into two groups for which regression with a linear function was carried out. Several combinations of the number of the datapoints in the two groups were explored, to find those for which the linear regression provided the best fit. The robust linear regression along a gnostic influence curve described in Section 2.2 was used to selecting fits with the smallest sum of squares of the regression residuals and the smallest number of outlying data in both groups. In this way, CALS of 5.6 was found from the intersection of the linear regression of the C_p^o/V data of the C1 to C4 (methyl- to butyl-substituted ILs) and C9 to C12 (nonyl- to dodecyl-

$$C_p^o/V = A_V + B_V n(C) \tag{13}$$

Table 12: Parameters A_{spec} and B_{spec} of the linear relationship Eq. 12 used to describe the specific heat capacity, C_p^o , at 298.15 K of the chiral ionic liquids [C_n-Im-CH₂OMen][Tf₂N] as a function of the number of carbon atoms in the alkyl group on the cation

$A_{spec}/ \mathrm{J} \cdot \mathrm{K}^{-1} \cdot \mathrm{g}^{-1}$	$B_{spec}/ \mathrm{J} \cdot \mathrm{K}^{-1} \cdot \mathrm{g}^{-1}$	$SEE \ 10^{27}/ \ J \cdot K^{-1} \cdot g^{-1}$
1.457	0.015	1.67

The value of CALS found for the present series of chiral ionic liquids is slightly lower than CALS=6 found by Rocha *et al.* for the achiral 1-alkyl-3-methylimidazolium

bistriflates. This slight discrepancy might be a result of a different data treatment, but also, considering the bulky (1R, 2S, 5R)-(-)-menthoxymethyl substituent on the N3 position of the imidazolium ring, this difference may be due to the slightly different regrouping on nanosegregation of the studied ionic liquids. However, when compared with the ionic liquids based on the 1-alkyl-3-methylimidazolium cation, the exchange of the methyl substituent for a bulkier and chiral menthoxymethyl one doesn't seem

to play a significant role in the observed structure-property relationships.

Table 13: Parameters A_V and B_V of the linear relationship Eq. 13 used to find the Critical Alkyl Chain Lenght from the specific heat capacity per unit volume, C_p^o/V , calculated from the smoothed density and specific heat capacity data of the chiral ionic liquids [C_n-Im-CH₂OMen][Tf₂N]

Alkyl substituent range	$A_V/ \mathrm{J}\cdot\mathrm{K}^{-1}\cdot\mathrm{g}^{-1}$	$B_V/\mathrm{J}\cdot\mathrm{K}^{-1}\cdot\mathrm{g}^{-1}$	$SEE~10^6/\rm{J}{\cdot}\rm{K}^{-1}{\cdot}\rm{g}^{-1}$
$(CH_3 \text{ to } C_4H_9)$	1.9712	-0.0097	7.1
$(C_9H_{19} \text{ to } C_{12}H_{25})$	1.9152	0.0003	0.2

5. Conclusion

A homologous series of chiral ionic liquids 3-alkyl-1-[(1R,2S,5R)-(-)-menthoxymethyl]imidazolium [Tf₂N] with alkyl ranging from methyl to dodecyl was characterized experimentally in terms of the refractive index, density, speed of sound, and isobaric heat capacity. Methods based on mathematical gnostics were used for the data treatment; measurements of the properties studied in this work for [hmim][Tf₂N] were assessed by the marginal analysis to estimate the measurement repeatability and the measured data were compared to available literature values to validate our measurements. The robust linear regression along a gnostic influence function was used to fit the parameters of the relationships used in this work. Using this robust algorithm, density and heat capacity data could be smoothed to better show the influence of the menthoxymethyl substituent on the cation on the measured properties. In this way, a trend shift related to changes in the nanostructuring due to the chang-

ing alkyl side-chain length similar to the one found by Rocha *et al.* in the 1-alkyl-3-methylimidazolium bistriflate homologous series could be established and a good

agreement between the CALS found in this work with that observed in their paper was observed. This shows that in 1-alkyl-3-R-imidazolium ionic liquids where R is an arbitrary functional group, the influence of the alkyl chain on the nanosegregation is

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principally influenced by the changing linear alkyl substituent rather than by the rest of the headgroup, regardless of the substituent on the N3 position. Compared with dialkylmethylimidazolium bistriflates, the chiral menthoxymethyl substituent thus does not appear to influence the coiling of the alkyl side-chain on the cation significantly.

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Fig. 1



Fig. 3



Fig. 5



Graphical abstract



Highlights

- A range of chiral ionic liquids with a natural terpene substituent was synthesized
- The studied ILs were characterized in terms of their physico-chemical properties
- Methods based on mathematical gnostics were used in the data analysis
- Nanosegregation in the studied range of ILs was estimated from heat capacity data

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