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Density, Thermal Expansion and Viscosity of Cholinium-Derived Ionic Liquids

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Density and viscosity data of the N-alkyl-*N*,*N*-dimethyl-*N*-(2-hydroxyethyl)ammonium bis(trifluoromethylsulfonyl)imide ionic liquids homologous series $[N_{1\ 1\ n\ 2(OH)}][Ntf_2]$ with $n=1$, 2, 3, 4 and 5 have been measured at atmospheric pressure in the $283<T/K<373$ temperature range and the corresponding isobaric thermal expansion coefficients have been calculated. This work studies the effect of increasing the alkyl chain length of the cholinium-based cation on the density, viscosity and related properties of this family of ionic liquids. A volumetric predictive method based on the effective molar volume of cations and anions is used to estimate the effective molar volume of the different cations present in this study. The results agree with data for other cation families that show a molar volume increment per CH_2 group on the alkyl chain of the cation of about 17.2 $cm^3\,mol^{-1}$, except for $[N_{1\ 1\ 1\ 2(OH)}]^+$, which exhibits an outlier behaviour. Molecular dynamics simulation results are used to explain the volumetric behaviour along the homologous series from a molecular perspective. The predictive power of group contribution methods for density and viscosity is also tested.

1. Introduction

Choline, *N*,*N*,*N*-trimethyl-*N*-(2-hydroxyethyl)ammonium chloride, is a water-soluble essential nutrient usually grouped within the B-complex vitamins. It can be found in food obtained from vegetables or animals, and supports several essential biological functions.[1] Studies show that this nutrient is especially important during pregnancy and lactation.[1–3] Moreover, Meck et al. and Jones et al. have observed that a choline-supplemented diet in rats play a critical role in brain development and memory function.[2,3]

Choline is used nowadays as a starting material for the development of environmentally friendly ionic liquids. The goal is to obtain ionic liquids that can unite the most relevant ionic liquid properties (such as a wide liquid range, non-flammability,[4] and negligible vapour pressure at ambient conditions)[5–7] with biocompatible properties. In this context, the presence of the hydroxyl group of the choline cation increases the biodegradability of the compound.[8]

Unfortunately, it is known that, for a given anion, ionic liquids based on the cholinium cation show higher melting points than those based on 1-alkyl-3-methylimidazolium cations.[9] Herein we have chosen bis(trifluoromethanesulfonyl)imide (bistriflimide) as the anion so that one could have a wider range of compounds in the liquid state at around room temperature. Our objective is to show the effect of increasing the alkyl chain length of one of the alkyl groups connected to the nitrogen in the cholinium cation in terms of density and viscosity.

Choline is thought to be safe for the environment and human health. However, care must be taken regarding the choice of the anion and the size/functionality of the alkyl side chains of the cation in order to preserve the "green" status of the final product. On one hand it is already known that, in combination with distinct cations, bistriflimide anions generally yield ionic liquids with relatively high toxicities.[10] Moreover, the increase of the length of the alkyl side chain also negatively affects toxicity, due to the increasing hydrophobicity of the ionic liquid.[11] There are already several studies dealing with the toxicity and biodegradability of cholinium-based ionic liquids with different anions.[12–16] However, only one of them[13] presents toxicity data for the bistriflimide anion, showing their higher toxicity when compared to that of their analogues halides. That study also shows the negative effect on toxicity of increasing the alkyl side chain in the cholinium cation.

Nevertheless, the scientific interest in cholinium-based ionic liquids is increasing as shown by several studies already published on possible applications, for example, in catalytic reactions,[17–21] as reaction media,[22] in processing of metals and metal oxides,[23] as crosslinking agents[24] or as protein handling media.[25] Only one study on the separation of aliphatic and aromatic compounds with $[N_{1\ 1\ n\ 2(OH)}][Ntf_2]$ has been found in the

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literature.[26] Studies of the volumetric and transport properties, namely, density and viscosity, of cholinium based ionic liquids are scarce due to the novelty of this family of ionic liquids, as well as their high melting temperature.[27] However, there are several papers that present the properties of mixtures of cholinium based ionic liquids with other solvents, like urea,[28] glycerol,[29] carboxylic acids[30] and others,[31,32] called deep eutectic solvents.

Herein, *N*-alkyl-*N*,*N*-dimethyl-*N*-(2-hydroxyethyl) ammonium bistriflimide ionic liquids, $[N_{1\,1\,n\,2(OH)}][Ntf_2]$ with $n=1,2,3,4$ and 5, were synthesised and their density and viscosity were measured within an extended temperature range, $283<T/K<373$. Several predictive/interpretative methods were used and, whenever necessary, new sets of parameters were calculated.[33–38]

2. Results and Discussion

2.1. Density

The experimental density data at atmospheric pressure for $[N_{1\,1\,1\,2(OH)}][Ntf_2]$, $[N_{1\,1\,2\,2(OH)}][Ntf_2]$, $[N_{1\,1\,3\,2(OH)}][Ntf_2]$, $[N_{1\,1\,4\,2(OH)}][Ntf_2]$ and $[N_{1\,1\,5\,2(OH)}][Ntf_2]$ are presented in Figure 1 and Table SI1 (Supporting Information). The results follow the expected behaviour along the homologous series, with a systematic decrease in density as the alkyl side chain of the cation increases.

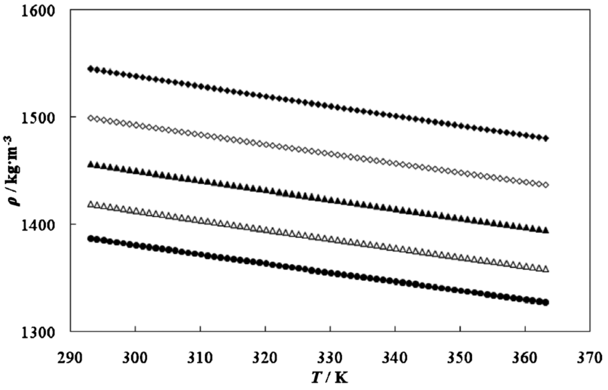


Figure 1. Experimental density data, ρ [kg m^{-3}], of ionic liquids with a common anion bis(trifluoromethanesulfonyl)imide, $[Ntf_2]^-$, and distinct *N*-alkyl-*N*,*N*-dimethyl-*N*-(2-hydroxyethyl)ammonium cations, $[N_{1\,1\,n\,2(OH)}]^+$, from 293.15 K to 363.15 K at atmospheric pressure: ◆, $[N_{1\,1\,1\,2(OH)}]^+$; ◇, $[N_{1\,1\,2\,2(OH)}]^+$; ▲, $[N_{1\,1\,3\,2(OH)}]^+$; △, $[N_{1\,1\,4\,2(OH)}]^+$; ●, $[N_{1\,1\,5\,2(OH)}]^+$.

To the best of our knowledge, there are no studies regarding the effect of temperature on density for this cholinium-based ionic liquid family. There is only one literature datum for the density of $[N_{1\,1\,2\,2(OH)}][Ntf_2]$ at 298.15 K with a value of 1.4974 g cm^{-3}, which is 0.2 % higher than our value.[39]

Some methodologies based on the concept of effective ionic volumes are extremely useful in predicting the density and molar volume of ILs. Despite the highly complex liquid structure of ILs, their volumetric properties have been shown to behave very close to ideality. For instance, binary mixtures of two ILs present quasi-zero excess volumes.[40] This feature led to the establishment[33–35] of a very simple, albeit very precise, rule-of-thumb for predicting the molar volume of any aprotic IL. The volume is taken as the sum of the effective volumes occupied by the constituent cations and anions ($V_m = V^*_c + V^*_a$). The typical predictive power of this algorithm is better than 0.5 %. In order to establish a scale of effective volumes of cations and anions, we had to anchor the value of a reference ion. From calculations based on atomic radii, we established a value of 73.7 cm^3 mol^{-1} for the effective volume occupied by $[PF_6]^-$ at 298.15 K.[33] Since the molar volume of the anion $[Ntf_2]^-$ is well defined within the scheme of estimated effective ionic radii,[33–35] measuring 158.7 cm^3 mol^{-1} at 298.15 K and atmospheric pressure, we used this methodology to predict the volumes of the distinct cations studied based on the Table SI1 (Supporting Information) experimental density values. The volumes of the distinct cations are shown in bold in Table 1.

Table 1. Effective size of several cations, V^*_c, and anions, V^*_a, at 298.15 K and 1 bar.[33–35,41–46]

IL Cation	V^*_c [cm^3 mol^{-1}]	IL Anion	V^*_a [cm^3 mol^{-1}]
$[C_0mim]^+$	64.8	$[Cl]^-$	25.9
$[C_2mim]^+$	99.2	$[Br]^-$	27.8
$[C_4mim]^+$	133.6	$[NO_3]^-$	39.1
$[C_6mim]^+$	168.0	$[CH_3CO_2]^-$	53.0
$[C_8mim]^+$	202.3	$[BF_4]^-$	53.4
$[C_{10}mim]^+$	236.7	$[PF_6]^-$	73.7
$[C_{12}mim]^+$	271.1	$[Ntf_2]^-$	158.7
$[(C_6)_3(C_{14})P]^+$	556.6	$[CH_3CH_2SO_4]^-$	91.4
$[N_{1114}]^+$	126.0	$[N(CN)_2]^-$	55.2
$[C_4mpyrro]^+$	144.3	$[HSO_4]^-$	53.3
$[C_3\text{-}3\text{-}C_1pyr]^+$	287.6	$[C_1SO_4]^-$	73.6
$[C_4\text{-}3\text{-}C_1pyr]^+$	304.6	$[C_2SO_4]^-$	91.7
$[C_4\text{-}4\text{-}C_1pyr]^+$	304.8	$[C_4SO_4]^-$	125.5
$[C_4pyr]^+$	287.4	$[C_6SO_4]^-$	159.5
$[C_6pyr]^+$	318.8	$[C_8SO_4]^-$	193.3
$[C_8pyr]^+$	355.4	$[FeCl_4]^-$	113.1
$[N_{1\,1\,1\,2(OH)}]^+$	**93.1**	$[C_1SO_3]^-$	66.5
$[N_{1\,1\,2\,2(OH)}]^+$	**107.8**	$[C_2SO_3]^-$	83.7
$[N_{1\,1\,3\,2(OH)}]^+$	**125.3**	$[C_4SO_3]^-$	117.9
$[N_{1\,1\,4\,2(OH)}]^+$	**142.7**	–	–
$[N_{1\,1\,5\,2(OH)}]^+$	**159.9**	–	–

The results show a CH_2 group increment of 17.36 cm^3 mol^{-1} for those ILs with an alkyl chain length longer than methyl, which perfectly matches the range of values found in the literature for this group of 17.2 ± 0.3 cm^3 mol^{-1}. This universal increase occurs irrespective of the chemical nature and position (cation or anion) of the substituted alkyl side chain.[35] The results also show that $[N_{1\,1\,1\,2(OH)}][Ntf_2]$ does not fit into this trend presenting instead a molar volume addition of only 14.7 cm^3 mol^{-1} when changing from $[N_{1\,1\,1\,2(OH)}][Ntf_2]$ to $[N_{1\,1\,2\,2(OH)}][Ntf_2]$.

The effective molar volume of distinct cations, V^*_c, and anions, V^*_a, available in the literature were merged with the results obtained in this work and are listed in Table 1.[33–35,41–46]

Other methods are available for estimating the density of ILs, namely the Ye and Shreeve method[36] and its extension proposed by Gardas et al.,[37] who use a group contribution method and Equation (1):

$$\rho = M/[NV(a + bT + cP)] \qquad (1)$$

in which ρ is the density in kg m^{-3}, M is the molar mass in kg mol^{-1}, N is the Avogadro constant, V is the molecular volume in m^3, T is the temperature in K and P is the pressure in MPa. The coefficients a, b and c are 0.8005 ± 0.0002, $6.652 \times 10^{-4} \pm 0.007 \times 10^{-4}$ K^{-1} and $-5.919 \times 10^{-4} \pm 0.024 \times 10^{-4}$ MPa^{-1}, respectively, at 95 % confidence level.[37]

The group contributions for the molecular volumes of the studied ILs were taken from the ref. [36] and are listed in Table 2.

Table 2. Comparison between the molecular volumes contributions from the literature[36] and those calculated using the Ye and Shreeve method.

Species	V m^{-3} Literature	Calculated
$[N_{1\,1\,1\,2(OH)}]^+$	1.72×10^{-28}	1.70×10^{-28}
$[N_{1\,1\,2\,2(OH)}]^+$	2.00×10^{-28}	1.95×10^{-28}
CH_2 in $[N_{1\,1\,n\,2(OH)}]^+$ with $n > 2$	2.80×10^{-29}	2.89×10^{-29}

To compare the predicted data with our experimental ones, we used the mean percent deviation (MPD) for i data points, given by Equation (2):

$$MPD[\%] = 100\Sigma_i \left|(\rho_{cal} - \rho_{exp})/\rho_{exp}\right|_i / i \qquad (2)$$

The MPD of the predicted density data were between 1.2 % and 0.5 %. Although a reasonable estimation of densities is achieved by this method, it is valuable to re-estimate new group contributions of each cation and consequently the CH_2 contribution based on experimental data. The group contribution parameters of the anion are well defined in the literature,[36] so only those of the cations were estimated. The calculation of the new group contribution parameters was performed by minimization of the MPD as defined in Equation (2). The molecular volume of the cholinium cation, $[N_{1\,1\,1\,2(OH)}]^+$, and the CH_2 group for the rest of the alkylcholinium-based family of ionic liquids, $[N_{1\,1\,n\,2(OH)}]^+$, with $n > 1$, were calculated and appear in Table 2. The MPD obtained with the new group contributions is smaller than 0.08 % for all ionic liquids used herein. It is interesting to note the agreement in CH_2 group contribution used in the density prediction (2.89×10^{-29} m^3·molecule^{-1} = 17.4 cm^3 mol^{-1}) with the one obtained recently for the series 1-ethyl-3-methylimidazolium alkylsulfate ($2.88 \cdot 10^{-29}$ m^3· molecule^{-1}).[40]

Table 3. Fitting parameters for density as a function of temperature using the quadratic polynomial equation [Equation (3)] for the studied ILs with a common anion bis(trifluoromethanesulfonyl)imide, $[Ntf_2]^-$, and distinct *N*-alkyl-*N*,*N*-dimethyl-*N*-(2-hydroxyethyl)ammonium cations, $[N_{1\,1\,n\,2(OH)}]^+$. All fittings have a correlation coefficient higher than 0.9999.

IL Cation	$A \pm \sigma_a$		$B \pm \sigma_b/10^4$ K^{-1}		$C \pm \sigma_c/10^7$ K^{-2}	
$[N_{1\,1\,1\,2(OH)}]^+$	7.5304	±0.0005	−7.220	±0.03	1.721	±0.05
$[N_{1\,1\,2\,2(OH)}]^+$	7.5062	±0.0005	−7.010	±0.03	1.389	±0.04
$[N_{1\,1\,3\,2(OH)}]^+$	7.4806	±0.0005	−7.163	±0.03	1.540	±0.05
$[N_{1\,1\,4\,2(OH)}]^+$	7.4565	±0.0005	−7.233	±0.03	1.562	±0.05
$[N_{1\,1\,5\,2(OH)}]^+$	7.4346	±0.0006	−7.275	±0.04	1.559	±0.06

2.2. Isobaric Thermal Expansion Coefficient

For all ionic liquids investigated, a simple first-order polynomial is insufficient to fit the data over the temperature range studied. Thus, a second-order polynomial equation was used to fit the ln(ρ) vs T data [Eq. (3)]:

$$\ln(\rho/kg\,m^{-3}) = A + B(T/K) + C(T/K)^2 \qquad (3)$$

where A, B and C are fitting parameters and T is the temperature in K. The parameters obtained allow for the calculation of the corresponding (α_p) values [Eq. (4)]. The A, B and C parameters for each ionic liquid, as well as the respective standard deviation, appear in the Table 3.

The isobaric thermal expansion coefficient, α_p, can be defined as the temperature derivative of ln(ρ) as expressed in Equation (4):

$$\alpha_p(K^{-1}) = -[\partial \ln\rho/\partial T(K)]_p = -[B + 2C(T/K)] \qquad (4)$$

The isobaric thermal expansion coefficients for this family of ionic liquids are shown in Figure 2. The use of a second-order polynomial function is warranted by the intrinsic precision along the densimetry runs, determined using an apparatus that allows for the measurement of density with five significant digits, corresponding to 0.001 % deviations. It must be stressed, however, that the overall uncertainty of the density measurements is estimated to be much higher (around 0.02 %) due to problems associated with the full characterization of the samples regarding their purity. The corresponding estimated overall uncertainty in the values of α_p is estimated at 2 %, but this fact does not preclude the following analysis of the α_p trends with temperature, evaluated from separate high-precision densimetry runs. Overall, the α_p values increase with the alkyl chain length of the cation.

The temperature dependence of the isobaric expansion coefficient is very small, with a negative slope in the studied temperature range. This behaviour is not anomalous, with other ionic liquids also presenting α_p values with very modest T-dependences and sometimes even minima in the α_p versus T plots not far from room-temperature.[40] For the $[N_{1\,1\,1\,2(OH)}][Ntf_2]$ the slope of the α_p with temperature is less ac-

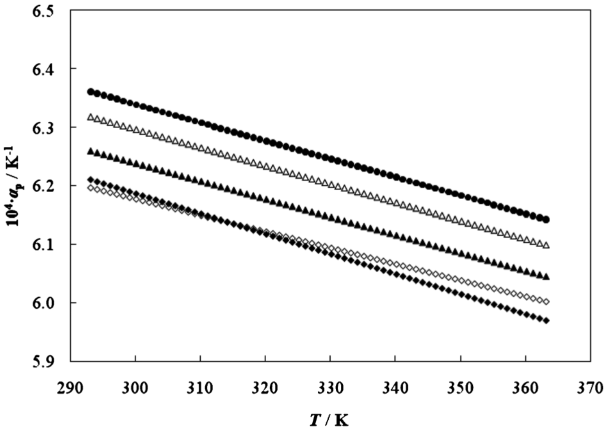


Figure 2. Isobaric thermal expansion coefficients, α_p/K^{-1}, of ionic liquids with a common anion bis(trifluoromethanesulfonyl)imide, $[Ntf_2]^-$, and distinct N-alkyl-*N*,*N*-dimethyl-*N*-(2-hydroxyethyl)ammonium cations, $[N_{1\,1\,n\,2(OH)}]^+$, from 293.15 K to 363.15 K at atmospheric pressure: ◆, $[N_{1\,1\,1\,2(OH)}]^+$; ◇, $[N_{1\,1\,2\,2(OH)}]^+$; ▲, $[N_{1\,1\,3\,2(OH)}]^+$; Δ, $[N_{1\,1\,4\,2(OH)}]^+$; ●, $[N_{1\,1\,5\,2(OH)}]^+$.

centuated than those of the other members of this IL family, suggesting that $[N_{1\,1\,1\,2(OH)}][Ntf_2]$ will reach its lowest α_p value at a lower temperature than the other ionic liquids within the series.

2.3. Structural Data from Molecular Dynamics Results

The outlying behaviour of $[N_{1\,1\,1\,2(OH)}][Ntf_2]$ within the series (already found in terms of predicted densities using the effective ionic volume scheme and exacerbated in the case of the thermal expansion trends with temperature) can be interpreted as a consequence of a different structural organization within the liquid. This issue can be investigated using atomistic simulations.

Molecular dynamics simulations have been extensively used to predict the complex structural organization of ionic liquids, where local charge ordering effects caused by the ubiquitous presence of the ions that form the polar network of the ionic liquid have to co-exist with non-polar domains composed of the alkyl moieties that are also present in some ions.[47] In the case of the cholinium cation and its alkylated derivatives, $[N_{1\,1\,n\,2(OH)}][Ntf_2]$ with $n=1$, 2, 3, 4 and 5, new simulations of the corresponding liquids have been performed at 298 K (Experimental Section). The equilibrated simulation trajectories have been used to calculate radial distribution functions (rdfs) for selected pairs of interaction centres within each system (Figure 3).

Figure 3 a shows the rdfs between the terminal carbon atoms (CT) of the longest unsubstituted alkyl chain of each cation. The first peaks (slightly above 0.4 nm) of this type of rdf are a fingerprint of the degree of segregation between the polar network and the non-polar domains. Even for $[N_{1\,1\,2\,2(OH)}][Ntf_2]$ there is already a non-negligible positive correlation between CT atoms. For $[N_{1\,1\,3\,2(OH)}][Ntf_2]$, $[N_{1\,1\,4\,2(OH)}][Ntf_2]$ and $[N_{1\,1\,5\,2(OH)}][Ntf_2]$, the association between CT groups becomes progressively more pronounced and for longer alkyl chains it is possible that such association might lead to the formation of a second continuous non-polar network, permeating the ever-present polar network. On the other hand for $[N_{1\,1\,1\,2(OH)}][Ntf_2]$ no first peak is clearly visible. In fact the methyl (or methylene) groups directly attached to the central nitrogen atom of tetra-alkylammonium cations can be regarded as still part of the polar network of the ionic liquid. Moreover, the symmetry of the three methyl chains in $[N_{1\,1\,1\,2(OH)}][Ntf_2]$ (as opposed to the non-symmetrical substitution for all other studied cases) implies that the polar network can interconnect in a more isotropic, compact way. This can be inferred from Figure 3 b, where the rdfs between selected charged interaction centres in the anion (NBT) and in the cation (N) are analysed. Whereas the cation–anion (NBT–N) show typical distances common throughout the entire homologous series [the two peaks of the rdf correspond to direct interactions between N and NBT (0.45 nm) and indirect interactions between those two atoms mediated by an oxygen atom of bistriflamide (0.60 nm)], the anion-anion distances (corresponding to the charge-ordered second shell of the polar network) are smaller for $[N_{1\,1\,1\,2(OH)}][Ntf_2]$ (0.80 nm) than for the remainder of the series (around 0.84 nm).

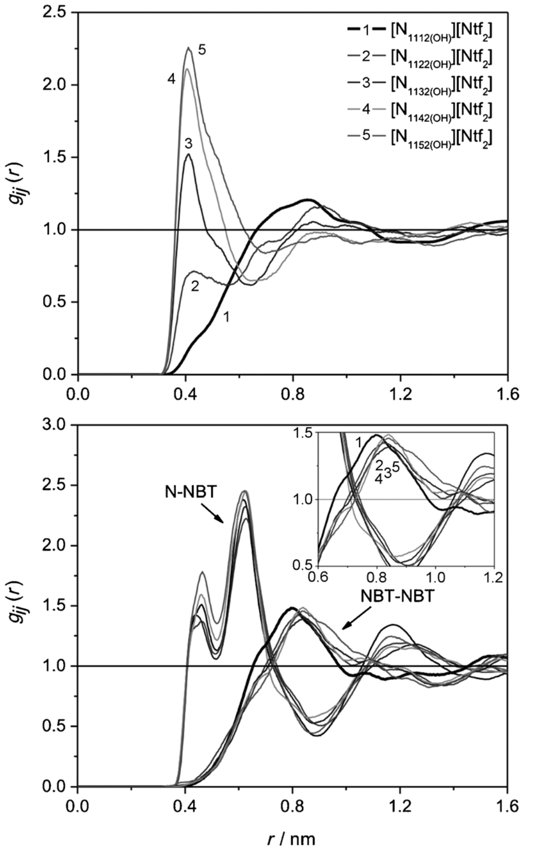


Figure 3. Radial distribution functions between selected pairs of interaction centres in pure $[N_{1\,1\,n\,2(OH)}][Ntf_2]$ with $n=1$, 2, 3, 4 and 5, ionic liquids: (a) CT–CT rdfs; (b) N–NBT and NBT–NBT rdfs. The out-of-phase behaviour of the rdfs of (b) signals the charge ordering effect imposed by the iconicity of the systems. The outlier behaviour of $[N_{1\,1\,1\,2(OH)}][Ntf_2]$ is highlighted using a thicker black curve in both figures.

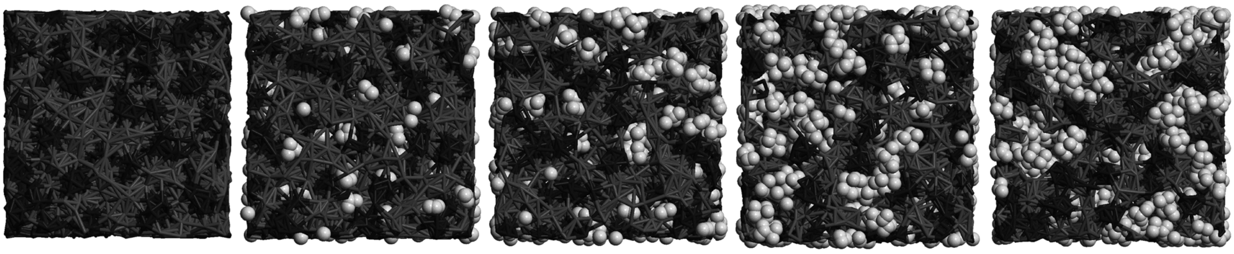


Figure 4. Selected snapshots of simulation runs in the systems (from left to right) $[N_{1\,1\,1\,2(OH)}][Ntf_2]$, $[N_{1\,1\,2\,2(OH)}][Ntf_2]$, $[N_{1\,1\,3\,2(OH)}][Ntf_2]$, $[N_{1\,1\,4\,2(OH)}][Ntf_2]$ and $[N_{1\,1\,5\,2(OH)}][Ntf_2]$. The colour coding highlights the presence of the polar network (anions, cations = dark grey) and the growth of non-polar domains in its midst (long non-substituted alkyl side chains of the cations = light grey).

Finally, the structural changes along the homologous series and their concomitant impact on the volumetric properties of the neat, bulk fluids can also be appreciated from a qualitative perspective using the sequence of color-coded snapshots presented in Figure 4. The appearance of small non-polar clusters containing the terminal atoms of the alkyl side chains only takes place from $[N_{1\,1\,2\,2(OH)}][Ntf_2]$ onwards. $[N_{1\,1\,1\,2(OH)}][Ntf_2]$ (a pure polar network) remains a true outsider in relation to this progression of increasingly larger non-polar pools dispersed in the continuous ionic liquid polar network.

2.4. Viscosity

Viscosity data, $\eta(T)$, for all studied ionic liquids are presented in Figure 5 and Table SI2 (Supporting Information). As expected, viscosity decreases with increasing temperature. The temperature-dependence of the data can be analysed using the Vogel-Fulcher-Tammann method represented by Equation (5),

$$\ln \eta = A_\eta + B_\eta / \left(T - T_{0\eta}\right) \tag{5}$$

where η is the viscosity in Pa·s, T is the temperature in K and A_η, B_η and $T_{0\eta}$ are adjustable parameters.

According to the literature,[38] the optimal value of $T_{0\eta}$ for the application of this correlation to ILs is 165.06 K. The A_η and B_η parameters are obtained using a group contribution method based on Equation (6).

$$\begin{aligned} A_\eta &= \Sigma_i n_i a_{i,n} \\ B_\eta &= \Sigma_i n_i b_{i,n} \end{aligned} \tag{6}$$

There are no parameters defined for the cholinium-based cations and their values were calculated using the fit to the experimental viscosity data and the available literature $a_{i,\eta}$ and $b_{i,\eta}$ values for the $[Ntf_2]$ anion.[38] The group contribution parameters for the cations as a whole are given in Table 4. The results show that a more refined group contribution method based on the addition of CH_2 groups is not recommended due to the non-monotonous behaviour of the viscosity data (Figure 6)—$[N_{1\,1\,1\,2(OH)}][Ntf_2]$ and $[N_{1\,1\,2\,2(OH)}][Ntf_2]$ are outliers and it would be spurious to try a fitting with just the remaining three cations. The use of this new group contribution parameterization allows us to correlate the viscosity data using the Vogel–Tammann–Fulcher method with an MPD between 0.1 % and 0.7 %.

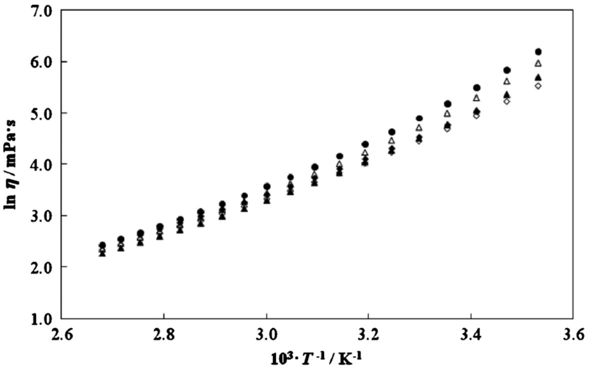


Figure 5. Experimental viscosity data, ln (η/mPa s), of ionic liquids with a common anion bis(trifluoromethanesulfonyl)imide, $[Ntf_2]^-$, and distinct *N*-alkyl-*N*,*N*-dimethyl-*N*-(2-hydroxyethyl)ammonium cations, $[N_{1\,1\,n\,2(OH)}]^+$, from 283.15 K to 373.15 K at atmospheric pressure: ◆, $[N_{1\,1\,1\,2(OH)}]^+$; ◇, $[N_{1\,1\,2\,2(OH)}]^+$; ▲, $[N_{1\,1\,3\,2(OH)}]^+$; △, $[N_{1\,1\,4\,2(OH)}]^+$; ●, $[N_{1\,1\,5\,2(OH)}]^+$.

Table 4. Group contribution parameters $a_{i,\eta}$ and $b_{i,\eta}$ calculated using the Vogel–Tammann–Fulcher method.

Species	$a_{i,\eta}$	$b_{i,\eta}$/K
$[N_{1\,1\,1\,2(OH)}]^+$	−7.54	773.68
$[N_{1\,1\,2\,2(OH)}]^+$	−7.64	776.33
$[N_{1\,1\,3\,2(OH)}]^+$	−8.05	840.94
$[N_{1\,1\,4\,2(OH)}]^+$	−8.21	892.85
$[N_{1\,1\,5\,2(OH)}]^+$	−8.32	931.55

Figure 6 shows the viscosity trends as a function of the unsubstituted alkyl side chain length, *n*, of the cation at two selected temperatures (298 K and 333 K). The viscosity data show non-monotonous behaviour at both selected temperatures, with viscosity minima at $[N_{1\,1\,2\,2(OH)}][Ntf_2]$ (298 K) and $[N_{1\,1\,3\,2(OH)}][Ntf_2]$ (333 K). The observed behaviour confirms the inadequacy of a general VTF method using a single $T_{0\eta}$ temperature to account for the trends along the homologous series (in other words, larger contributions from more CH_2 groups along the series cannot account for the non-monotonous behaviour of the trends).

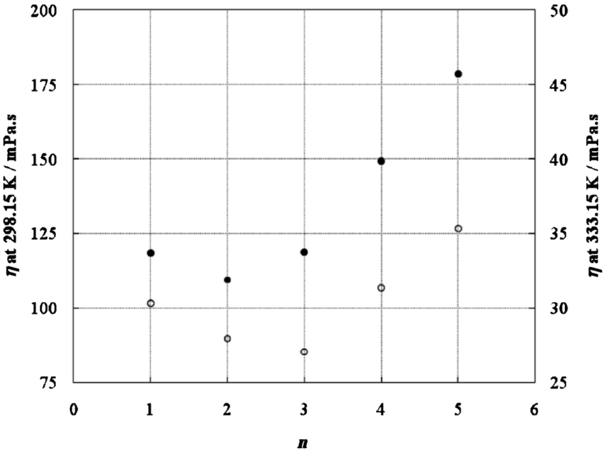


Figure 6. Experimental viscosity values, (η/mPa s), of ILs with a common anion bis(trifluoromethanesulfonyl)imide, [Ntf2]-, and distinct *N*-alkyl-*N*,*N*-dimethyl-*N*-(2-hydroxyethyl)ammonium cations, $[N_{1\,1\,n\,2(OH)}]^+$ at atmospheric pressure: ●, at 298.15 K; ○, at 333.15 K.

As in the case of the volumetric properties, the dynamics along this particular homologous series are also a consequence of the complex nature of the systems. Apart from the structural heterogeneities at a molecular level discussed in the previous section, one also has to consider the delicate balance between the electrostatic interactions characteristic of ionic media, the progressively stronger van der Waals interactions between the alkyl side chains of the cations, the possibility of hydrogen-bonding via the hydroxyl groups of the choline cation (with the oxygen atoms of the anion but also with other hydroxyl groups of other cations), and even the presence of weak van der Waals interactions between the terminal trifluoromethyl groups of the bistriflamide anion. All these interactions will exhibit differentiated temperature dependences[27] and their relative strength will be a function of the degree of polar-to-non-polar ratio along the homologous series.[47,48]

3. Conclusions

Density and viscosity data of *N*-alkyl-*N*,*N*-dimethyl-*N*-(2-hydroxyethyl)ammonium bis(trifluoromethanesulfonyl)imide ionic liquids, with alkyl side chain $n=1$, 2, 3, 4 and 5 from 283.15 up to 373.15 K were measured. The objective was to study the effect of increasing the alkyl chain length of the cholinium-based cation on the density, viscosity and related properties of this family of ionic liquids. As expected, density decreases as the alkyl chain length of the cation increases while a more complex behaviour was found for viscosity. Thermal expansion coefficients were calculated from the measured density data and for the $[N_{1\,1\,1\,2(OH)}][Ntf_2]$ the slope of the α_p with temperature is less negative than those of the others members of this IL family.

The increase obtained in molar volume of 17.28 cm^3 mol^{-1} per CH_2 group added to the alkyl chain of the cation compares well with the literature value except for $[N_{1\,1\,1\,2(OH)}][Ntf_2]$. The Ye–Schreeve group contribution method was used to estimate density. No group contribution parameters for the cation were found in the literature for the estimation of viscosity by the Vogel–Tammann–Fulcher method. New contribution group parameters were derived for both methods, despite the reasonable agreement of density data using the Ye–Schreeve method.

Molecular dynamics studies show that the existence of small non-polar clusters containing the terminal atoms of the alkyl side chains only takes place from $[N_{1\,1\,2\,2(OH)}][Ntf_2]$ onwards. This structural change along the series is at the origin of the non-conformal behaviour of $[N_{1\,1\,1\,2(OH)}][Ntf_2]$ within the studied series of ionic liquids.

Experimental Section

Chemicals

The *N*-alkyl-*N*,*N*-dimethyl-*N*-(2-hydroxyethyl)ammonium bistriflimide ionic liquids, $[N_{1\,1\,n\,2(OH)}][Ntf_2]$ with $n=1$, 2, 3, 4 and 5, used herein were synthesised using the procedures described below.

Commercially available reagents with analytical grade quality were used as received. Lithium bistriflimide ($LiNtf_2$) (mole fraction purity 99%) was purchased from IoLiTec. 1-bromoethane, 1-bromopropane, 1-bromobutane and 1-bromopentane, all with mole fraction purity $\geq$99% and dimethylaminoethanol with a mole fraction purity $\geq$98% were purchased from Sigma–Aldrich.

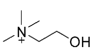
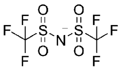
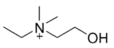
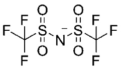
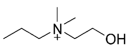
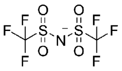
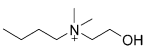
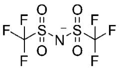
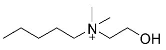
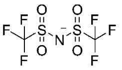
The salts $[N_{1\,1\,n\,2(OH)}][Br]$ were prepared first. The alkyl halide ($C_nH_{2n+1}Br$, $n=2$, 3, 4, 5) (1.1 mol equiv.) and 2-dimethylaminoethanol (1.0 mol equiv.) were mixed in round-bottomed flask, dissolved in *n*-hexane, under vigorous stirring, warmed-up to 80 °C under reflux and N_2 atmosphere for several hours (monitored by ^{1}H NMR). The formation of the product can be observed by its precipitation from *n*-hexane. After completion of the reaction, the mixture was then filtered and the reaction product was washed extensively with *n*-hexane in order to remove unreacted compounds and then dried under vacuum. The resulting $[N_{1\,1\,n\,2(OH)}][Br]$ (yield 96–99%) was used without further purification.

The synthesis of the $[N_{1\,1\,n\,2(OH)}][Ntf_2]$ series was then performed by a metathesis reaction between the corresponding $[N_{1\,1\,n\,2(OH)}][Br]$ (1.0 equiv) and a slight excess of $LiNtf_2$ (1.05 equiv). In a typical reaction, 25 mL of $LiNtf_2$ (5.25 M in water) was added, at room temperature, to an equal amount of a stirred solution of $[N_{1\,1\,n\,2(OH)}][Br]$ (5.0 M in water). The mixture was stirred for an additional 30 min, then extracted with dichloromethane (3×15 mL), and washed with doubly-distilled deionized water (MilliQ) (3×5 mL). After evaporation of the solvent, the product obtained was dried under vacuum. The same procedure was adopted for the synthesis of $[N_{1\,1\,1\,2(OH)}][Ntf_2]$, but using as a reagent a commercial sample of $[N_{1\,1\,1\,2(OH)}][Cl]$, which was supplied by Sigma Aldrich with a stated purity better than 98%.

Table 5 lists the ILs, their respective acronyms and chemical structure. Proton NMR spectra were recorded with a BRUKER Avance 400 Ultrashield Plus spectrometer, operating at 400 MHz and 298 K. The spectra, given in Table SI3, confirmed purity levels better than 99% for all synthesised samples.

In order to reduce water and volatile compounds to negligible values, all samples were dried under vacuum (0.1 Pa) and vigorously stirred at moderate temperature (330 K) for at least a day immediately before their use. Coulometric Karl-Fischer titrations revealed levels of water, always below $\delta=300$ ppm. It must be stressed that cholinium-based ionic liquids (even when combined with hydrophobic anions such as $[Ntf_2]^-$) tend to be more hydrophilic than

Table 5. Acronyms and chemical structures of the ILs studied herein. Other acronyms used throughout the text (not depicted) include the cations: $[C_n\text{mim}]^+ = $ 1-alkyl-3-methylimidazolium; $[P_{6\,6\,6\,14}]^+ = $ trihexyl-tetradecyl-phosphonium; $[N_{1\,1\,1\,4}]^+ = $ trimethyl-butylammonium; $[C_4\text{mpyrro}] = $ *N*-buty-*N*-methylpyrrolidinium; $[C_n\text{-3-}C_1\text{pyr}]^+ = $ 1-alkyl-3-methylpyridinium; $[C_4\text{-4-}C_1\text{pyr}]^+ = $ 1-butyl-4-methylpyridinium; and $[C_n\text{pyr}]^+ = $ N-alkylpyridinium.

Ionic Liquid	Acronym	Cation	Anion
N,*N*,*N*-trimethyl-*N*-(2-hydroxyethyl)ammonium bis(trifluoromethanesulfonyl) imide	$[N_{1\,1\,1\,2(OH)}]$ $[Ntf_2]$		
N-ethyl-*N*,*N*-dimethyl- *N*-(2-*h*ydroxyethyl)ammonium bis(trifluoromethanesulfonyl) imide	$[N_{1\,1\,2\,2(OH)}]$ $[Ntf_2]$		
N-propyl-*N*,*N*-dimethyl- *N*-(2-*h*ydroxyethyl)ammonium bis(trifluoromethanesulfonyl) imide	$[N_{1\,1\,3\,2(OH)}]$ $[Ntf_2]$		
N-butyl-*N*,*N*-dimethyl- *N*-(2-*h*ydroxyethyl)ammonium bis(trifluoromethanesulfonyl) imide	$[N_{1\,1\,4\,2(OH)}]$ $[Ntf_2]$		
N-pentyl-*N*,*N*-dimethyl- *N*-(2-*h*ydroxyethyl)ammonium bis(trifluoromethanesulfonyl) imide	$[N_{1\,1\,5\,2(OH)}]$ $[Ntf_2]$		

their imidazolium-based counterparts. Titrations for $[N_{1\,1\,1\,2(OH)}][Ntf_2]$ (the most hydrophilic of the studied ionic liquids) have yielded $\delta =$ 164, 142 and 117 ppm after different experiences/recovery cycles. The stated value of $\delta = 300$ ppm is a conservative estimate that takes into account the uncertainty associated with the handling of the samples.

Densimetry

The density measurements were performed at atmospheric pressure with an Anton Paar vibrating tube densimeter, model DMA 5000, at temperatures ranging from 293 K to 363 K. The densimeter was internally calibrated by measuring the densities of atmospheric air and bi-distilled water, according to the manufacturer's recommendations. The DMA 5000 cell is embedded in a cavity inside a metal block, controlled for temperature by several Peltier units resulting in a temperature stability better than ±2 mK for periods over 10 min. Under these operating conditions, the density measurement was repeatability better than 0.04 kg m^{-3} and the expanded uncertainty was estimated to be $\pm 0.3\ \text{kg m}^{-3}$. All reported density data were corrected for the viscosity effect using the internal calibration of the densimeter.

To prevent any contamination by water or air bubbles, we filled a syringe with (ca. 2 cm^3) of the liquid under nitrogen flow and injected it into the densimeter. Three samples (from different sections of the syringe) were measured at 293 K and if the density values agreed within 0.04 kg m^{-3}, the last sample was used to measure the density for the entire temperature range.

Viscosimetry

Measurements of viscosity were performed using an automated SVM 3000 Anton Paar rotational Stabinger viscometer-densimeter. The device uses Peltier elements for fast and efficient thermostatization. Temperature uncertainty is ±0.02 K. The precision of the dynamic viscosity measurements is ±0.5%. The overall uncertainty of the measurements (taking into account the purity and handling of the samples) is estimated to be 2%.[49]

Measurements were carried out at temperatures between 283.15 and 373.15 K at atmospheric pressure. At least 3 measurements were performed for each IL and the reported result is the average value with a mean deviation smaller than 1.0%.

Molecular Dynamics Simulations

Molecular dynamics simulations were carried out for all ionic liquids in this work. The simulations were performed using the DL_ POLY code[50] and an all-atom force field based on the CLaP force-field,[51,52] specially tailored to encompass this and other ionic liquid homologous series. For each ionic liquid herein, we started from low-density initial configurations composed of 150 ion pairs. The boxes were equilibrated under isothermal-isobaric ensemble conditions for 700 ps at 300 K using the Nosé–Hoover thermostat and isotropic barostat with time constants of 0.5 and 2 ps, respectively. Further simulation runs of 300 ps each and a total simulation time above 1.6 ns were used to produce equilibrated systems at the studied temperature. Electrostatic interactions were treated using the Ewald summation method considering six reciprocal-space vectors, and repulsive-dispersive interactions were explicitly calculated below a cutoff distance of 1.6 nm (long-range corrections were applied assuming the system has an uniform density beyond that cutoff radius). Details concerning this type of simulation can be found elsewhere.[51,52]

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Keywords: choline · density · ionic liquids · molecular dynamics simulations · viscosity

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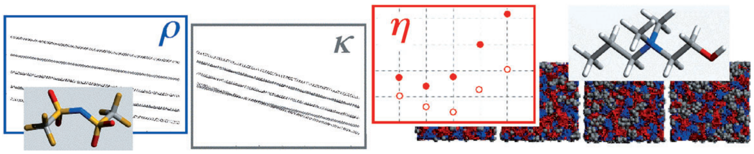

Density, thermal expansion coefficient and viscosity data are reported for cholinium-based ionic liquids of the *N*-alkyl-*N*,*N*-dimethyl-*N*-(2-hydroxyethyl)-ammonium bis(trifluoromethylsulfonyl)imide series (see picture). The outlier character of the first member of the homologous series is interpreted at a molecular level by means of MD simulations.

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■■–■■

Density, Thermal Expansion and Viscosity ofCholinium-Derived Ionic Liquids