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Cholinium-Amino Acid based Ionic Liquids: a new method of synthesis and physico-chemical characterization.

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In the present work we report the synthesis and physico-chemical characterization in term of viscosity and density of a wide series of cholinium-amino acid based room temperature ionic liquids ([Ch][AA] RTILs). 18 different amino acids were used obtaining 14 Room Temperature ILs. Among the most common AA, only Valine did not form an RTIL but is liquid above 80 °C. With respect to the methods reported in the literature we propose a synthesis based on a potentiometric titration which has several advantages such as shorter preparation time, stoichiometry within ± 1%, very high yields (close to 100 %), high reproducibility, no use of organic solvents, thus resulting more environmentally friendly. We tried to prepare dianionic ILs with some AAs with two potentially ionisable groups but in all cases the salts were solid at room temperature. All the ILs were characterized by ^{1}H NMR to confirm the stoichiometry. Physico-chemical properties such as density, viscosity, refractive index and conductivity were measured as a function of temperature and correlated with empirical equations. The values were compared with the data already reported in literature for some [Ch][AA] ILs. The thermal expansion coefficients α_p and the molar volume V_m were also calculated from the experimental density values. Due to the high number of AAs explored and their structural heterogeneity we have been able to find some interesting correlations between the data obtained and the structural feature of the AAs in terms of alkyl chain length, hydrogen bonding ability, stacking and cyclization. Some parameters were also found to be in good agreement with those reported for other ILs. We think that this data can give an important contribution to the understanding of the structure-properties relationship of ILs also because focused on the structure effect of the anion, while most data in the literature are referred to the cations.

Introduction

Due to their interesting characteristics as low vapour pressure, nonflammability, high thermal and chemical stability, outstanding solvent capacity and recyclability, ionic liquids (ILs) have attracted more attention in recent years to be used in many fields such as electrochemistry, solvents for synthesis, catalysis, extraction, gas separation, and so on.[1-4] Despite ILs are usually seen as green solvents, the traditional imidazolium and pyridinium based ILs demonstrated not to have good biodegradability and biocompatibility and are usually obtained from non-renewable sources.[5,6] Among the most abundant biomaterials to be used as component in ILs, amino acids, due to their nontoxicity, biodegradability and biocompatibility, have to be considered as excellent feedstock for the synthesis of ILs. The first synthesis of 20 ionic liquids obtained from natural amino acids (AAILs) and 1-ethyl-3-methylimidazolium (EMIM) cation was reported by Fukumoto's group.[7] One of the best candidate cation for the preparation of highly biocompatible AAILs is choline, an essential micronutrient for all cells. For example, Elliott and Weaver found that choline phosphate ILs exhibit excellent biocompatibility and biodegradability.[8] The first synthesis of [Ch][AA] ILs was reported in 2010 by Calvino-Casilda and co-workers.[9] They successfully used these [Ch][AA] ILs as catalysts for the Knoevenagel condensation reactions between benzaldehyde and different active methylene compounds. Then, Liu et al. exploited these ILs for the selective extraction of lignin from lignocellulosic materials obtaining excellent results using the [Ch][Gly] IL as a solvent.[10] Therefore, to study the potential of such AAILs to be applied in various fields of chemical industry, the knowledge of their physico-chemical properties is very important. In their work, Liu et al. reported data on glass transition temperature (T_g), decomposition temperature (T_d) and viscosity (η) of 18 [Ch][AA] ILs.[10]In 2013, Tao et al. reported a detailed physicochemical characterization of 5 [Ch][AA] ILs.[11] They reported the values of T_g and T_d and the temperature dependence of viscosity (η), density (ρ), conductivity (σ) and refractive index (n_D). Comparing data of these two manuscripts important differences between some [Ch][AA] ILs can be observed. For instance, Tao et al. obtained $\eta_{25\ °C}$ = 182, 385.6, 10644 and 11544 mPa·s for [Ch][Gly], [Ch][Ala], [Ch][Pro] and [Ch][Ser], respectively while Liu et al. obtained 121, 163, 500 and 402 mPa·s, respectively. The values of [Ch][Pro] and [Ch][Ser] reported in the two manuscripts are completely different (more than one order of magnitude). This could be due to some problems in the synthesis that prevent to obtain reproducible chemical physical properties of [Ch][AA] ILs or to important differences in the amount of residual water. In fact, ILs are usually highly hygroscopic and can easily absorb significant amounts of water[12-14] that, as already observed for other ILs, can significantly affect the value of viscosity.[13-15]

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Therefore, in order to contribute to elucidate the correlation of viscosity and density with the structure and molecular weight of ILs in this manuscript we will report the physico-chemical characterization of 13[Ch][AA] ILs with very different structural features. We will report data on the dependence of density, viscosity, refractive index and conductivity on temperature. In order to make the synthesis as reproducible as possible and, therefore, to obtain reproducible physico-chemical data, we will propose a different method of preparation that avoid the use of organic solvents and increase the yield of the final product.

Experimental section

Materials

Glycine (Gly), L-alanine (Ala), L-serine (Ser), L-proline (Pro), L-isoleucine (Ile), L-lysine (Lys), L-cysteine (Cys), L-methionine (Met), L-histidine (His), L-phenylalanine (Phe), L-leucine (Leu), L-aspartic acid (Asp), L-glutamic acid (Glu), L-Tyrosine (Tyr), L-valine (Val), L-norvaline (Nva), L-norleucine (Nle) were Fluka products (purity ≥ 99 %) and L-homophenilalanine (Hph) were used as received. Choline hydroxide (aqueous solution 46 wt%, Sigma) was purchased from Sigma Aldrich. Methanol and acetonitrile were of analytical grade and used without any further purification. Doubly distilled water was used in all experiments**.**

Methods

Synthesis of [Ch][AA] ILs

First method: we used, with slight variations, the method reported in the literature.[10,11][Ch][OH] aqueous solution (about 4 M) was added dropwise with cooling to an amino acid aqueous solution or suspension (0.06 mol) in order to obtain a slightly excess (about 10 mol%) of amino acid. The mixture was stirred at about 3 °C overnight in the dark. Water was then removed under reduced pressure at 50 °C with a rotavapor. Acetonitrile/methanol (9:1, v/v) was then added with vigorous stirring in order to precipitate the excess of amino acid. The mixture was left stirring overnight and the excess of amino acid was then filtered off. Filtrate was evaporated to remove solvents at 50 °C. The product was dried *in vacuo* for 24 h at 50 °C.

Second method: this method is based on a potentiometric titration. [Ch][OH] aqueous solution (20 mL, about 2.5 M) was titrated by adding small amounts of solid AA under stirring at about 3 °C. Between each AA aliquot we waited to obtain complete solubilization of AA (usually less than 1 min). In the proximity of the equivalence point each AA addition was reduced to about 1 mol% of the stoichiometric amount required for titration. This was the best compromise to obtain good S/N ratio in the derivative of pH ($\Delta pH/\Delta n_{AA}$) and a maximum error of ±1mol% in the determination of the equivalence point. An excess of about 10-15 mol% of AA was added beyond the equivalence point. The excess of AA was lower for AAs with very low solubility in water. The excess of AA was back titrated by adding a volume of [Ch][OH] with the same concentration of the starting [Ch][OH] solution calculated as follow:

$$V_{[Ch][OH]_{bt}} = \frac{V_{[Ch][OH]_{start}} \cdot n_{AAexc}}{n_{AA_{ep}}} \quad 1$$

where $V_{[Ch][OH]bt}$ is volume of [Ch][OH] for back titration, $V_{[Ch][OH]start}$ is the initial volume of [Ch][OH], n_{AAep} are the moles of AA necessary to reach the equivalence point and n_{AAexc} are the moles of AA added in excess beyond the equivalence point. Water was then removed under reduced pressure at 50 °C. The product was dried *in vacuo* for 24h at 50 °C under stirring. For AAs having a second acid group (Asp, Glu, Tyr, Cys) the equivalence point corresponds to the formation of a dianionic salt $[Ch]_2[AA]$. This was obtained with the same procedure reported above. To obtain the monoanionic salt [Ch][AA] the total amount of AA added was twice that necessary to reach the equivalence point. Structure of the resulting [Ch][AA] ILs was confirmed by ^{1}H NMR spectroscopy. The water content of most amino acid ionic liquids, determined with a Karl Fischer moisture titrator (831 KF Coulometer Metrhom),was less than 0.2 wt %.

^{1}H and ^{13}C NMR measurements.

Spectra were recorded at 298 K on a Varian XL-300 spectrometer operating at 300 MHz. Solutions were prepared by dissolving 20-30 mg of IL in 0.7 mL of D_2O.

Density measurements.

Density measurements were conducted using a DM45 Mettler-Toledo density-meter equipped with a vibrating tube. The precision of the instrument was 10^{-5} g/mL. The temperature was controlled up to 10^{-3} K by means of a Peltier module. The density meter was calibrated with dry air and degassed–bidistilled water at ambient pressure and temperature. Density was measured over the temperature range 293.15 - 343.15 K with a control accuracy of ± 0.05 K.

Refractive Index Measurements.

The refractive indices of all samples were determined using a Rudolph research analytical J257 refractometer with a measuring accuracy of ± 0.0001 in the temperature range 293.15 - 333.15 K with a control accuracy of ± 0.05 K. The apparatus was calibrated before each series of measurements and checked using pure organic solvents with known refractive indices.

Viscosity measurements

Measurements were carried out with a Bohlin CS10 stress controlled rheometer equipped with a water based thermostat (± 0.1 °C) using a cone-plate measuring system (CP 4/40). About 1.3 mL of IL were loaded in the measuring system. The measuring geometry was isolated by a homemade box fluxed with Argon in order to prevent moisture absorption. Temperature dependence was measured in the range 293.15 - 333.15 K with a control accuracy of ± 0.05 K. The thermal equilibrium time was about 15 min.

Conductivity measurements:

Measurements were carried out using a Crison Basic 30 conductimeter equipped with an EC 5073 electrode. The measuring test tube containing the IL and the electrode was fluxed with Argon during the measurements. Temperature dependence was measured in the range 293.15 - 343.15 K with an accuracy of ± 0.05 K. The thermal equilibrium time was about 15 min.

Results and discussion

Synthesis

The significant differences between the viscosity data reported by Liu et al.[10] and Tao et al[11] suggested us that some issues could be present in the synthesis. As a matter of fact, using the method reported in the literature, for some AAs (for example [Ch][Gly]

[Ch][leu] [Ch][His]) we observed problems such as precipitation of the AA during the rotavapor evaporation of water or in the final anhydrification step or precipitation after a few days. However, [Ch][Ala], [Ch][Ser] and [Ch][Phe] were prepared without problems, NMR confirmed stoichiometry and their viscosity values where similar to the values obtained for the [Ch][AA]ILs prepared with the titration method (within ± 10 %). We used a potentiometric titration method that employs the solid AAs to titrate [Ch][OH]. It is necessary to add the solid AA to [Ch][OH] because most AAs are only slightly soluble in water while the AA anion formed after reaction with [Ch][OH] is usually soluble in water at least for 10 - 15 mol% excess of AA. Only in few cases ([Ch][Leu], [Ch][Ile], [Ch][Nle]) it was necessary to reduce the excess of AA to prevent precipitation.

The potentiometric titration curve and its derivative for [Ch][Gly] is reported in Figure 1. The structure of all [Ch][AA] ILs and their 1:1 stoichiometry was confirmed by ^{1}H and ^{13}C-NMR (see Supporting Information). ^{1}H-NMR spectra of different preparations of the [Ch][AA]ILs were always perfectly superimposable and in quantitative agreement, confirming the reproducibility of the synthesis. The yields (calculated with respect to the moles of AA used in the titration) were always higher than 90% and often close to 95-100% (Table 1).

Table 1 Yields, viscosity (η), density (ρ), refractive index (n_D) and conductivity (σ) values at 25 °C for [Ch][AA] ILs at Pressure p = 0.1 MPa.

[Ch] [AA]	Yelds	η (Pa·s)	ρ (g·cm^{-3})	n_D	σ (μS·cm^{-1})
[Ch][Gly]	96%	1.23	1.15560	1.5012	90.60
[Ch][Ala]	92%	0.72	1.12998	1.4958	74.10
[Ch][Val][a]	-	-	-	-	-
[Ch][Nva]	99%	5.18	1.07485	1.4891	30.03
[Ch][Leu]	90%	7.98	1.05192	1.4882	12.36
[Ch][Ile]	90%	11.20	1.06846	1.4892	10.61
[Ch][Nle]	98%	6.43	1.05125	1.4865	20.44
[Ch][Ser]	95%	12.5	1.20109	1.5060	17.46
[Ch][Lys]	91%	187	1.15224	1.5147	0.84
[Ch][Cys]	95%	31.2	1.18042	1.5278	1.98
[Ch][Met]	93%	4.30	1.14490	1.5220	42.69
[Ch][Pro]	92%	9.81	1.13770	1.5074	7.53
[Ch][His]	98%	7063	1.20402	1.5387	0.12
[Ch][Phe]	94%	55.3	1.14289	1.5408	4.35
[Ch][Hph]	96%	36.8	1.12005	1.5381	5.76

[a] Valine did not form an RTIL but is liquid above 80 °C.

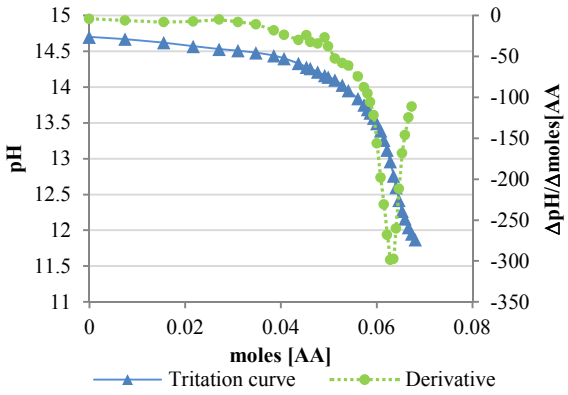

Figure 1 Potentiometric titration curve and its derivative for [Ch][Gly] starting from 22mL of about 2.7 M [Ch][OH] solution (0.0594 mol).

Considering that there are not steps that should cause loss of product, we think that the main reason for lowering yields is the hydration of the AA. It has to be underlined that for this method it is not necessary to know exactly the concentration of [Ch][OH] or the hydration degree of AAs.

[Ch][Val] was solid at room temperature but was liquid above about 80 °C. This is quite surprising being the only AA of the alkyl series that did not give a RTIL. We can tentatively explain this result in terms of balance of inductive effect of the alkyl chain and possible segregation of it in hydrophobic domains. It has already been demonstrated[16,17] that with respect to Gly and Ala, Val, owing to the greater +I effect of alkyl chain, induces an increase of negative charge density on the carboxylic group of the amino acid that increases the interactions with other cations or solvents. Furthermore, the iso-propyl group is probably too compact to be able to segregate in well separated hydrophobic domain as could be able to do AAs with longer alkyl chains (Leu, Ile, Nle) or Nva having the same number of carbon atoms but in a linear chain.

For AAs having a second acid group (Asp, Glu, Tyr, Cys) the product obtained at the equivalence point corresponds to the dianionic salt [Ch]$_2$[AA]. The monoanionic salt [Ch][AA] was obtained by adding to the same amount of [Ch][OH] twofold molar excess of AA with respect to that used for the equivalence

point. Particular attention has been paid to Cysteine that could give rise to dimerization or degradation during the preparation. The ^{1}H- and ^{13}C-NMR spectra (see Supporting Information) demonstrate the integrity of the cysteinate anion.

Table 2 Physical state of $[Ch]_2[AA]$ and [Ch][AA] salts prepared with AAs having a second acid group.

	Temperature	
$[Ch]_x[AA]$	**25 °C**	**90°C**
$[Ch]_2[Asp]$	Solid	Solid
[Ch][Asp]	Solid[a]	Liquid
$[Ch]_2[Glu]$	Solid	Solid
[Ch][Glu]	Solid[a]	Liquid
$[Ch]_2[Tyr]$	Solid	Liquid[c]
[Ch][Tyr]	-[d]	-[d]
$[Ch]_2[Cys]$	Solid[b]	Solid[b]
[Ch][Cys]	Liquid	Liquid

[a] glassy, [b] waxy solid, [c] highly viscous, [d] this salt was not obtained due to precipitation during the synthesis.

It was not possible to prepare [Ch][Tyr] due to precipitation during second step of titration. [Ch][Asp] and $[Ch]_2[Tyr]$ were solid at 25 °C but liquid at 90 °C and therefore can be defined ILs but not RTILs. Therefore we can conclude that RTILs of dianionic AAs cannot be prepared. Of the corresponding monoanionic AA salt, only [Ch][Cys] was a RTILs, [Ch][Asp] and [Ch][Glu] were ILs only at 90 °C.

Viscosity measurements

The shear rate dependence of viscosity is reported in Figure 2. Viscosity of all [Ch][AA] ILs were independent on the shear rate showing a Newtonian behaviour as expected for ILs. Viscosity values are reported in Table 1.

Viscosities cover a wide range from the lower value of [Ch][Ala] (0.72 Pa·s) to the higher value of [Ch][His] (7063 Pa·s) and are significantly higher than the viscosities of most common ILs. If compared with the values measured for the same [Ch][AA] ILs by other authors our values are in reasonable agreement with those reported by Tao et al.[10] for [Ch][Pro] and [Ch][Ser] (differences less than 10 %) while the differences are more pronounced for [Ch][Gly] (one order of magnitude higher) and [Ch][Ala] (more or less twice). Our data are significantly higher than most of the values reported by Liu et al,[11] for some ILs being higher of two orders of magnitude. As expected, the values measured by Muhammad et al.[19] for [EMIM][Gly] (61 mPa·s), [EMIM][Ala] (171 mPa·s), [EMIM][Pro] (426 mPa s) and [EMIM][Ser] (411 mPa·s) are significantly lower than the values we obtained for the corresponding [Ch] based ILs.

It has been demonstrated that the viscosity of ILs depends on molecular weight, structure and symmetry of cations and, especially, anions.[18-21] In order to highlight correlations with the structure of AA, viscosity data have been reported as a function of AA molecular weight (Figure 3). It has to be underlined that the variation of the viscosity measured for different preparations of the same IL was always less than ± 8%; in the semi-log graph of Figure 3 the error bars are smaller than the symbols used for the points. This confirm the reproducibility of our synthetic method considering that viscosity is very sensitive to the presence of impurities and water. The presence of side groups that can give rise to van der Waals, stacking and hydrogen bonding interactions in the studied AAs makes it difficult to obtain a single trend but we identified two

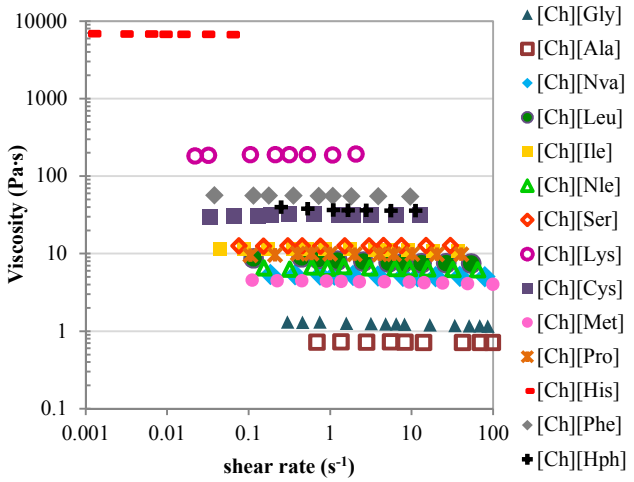

Figure 2 Shear rate dependence of viscosity of [Ch][AA] ILs at 25 °C.

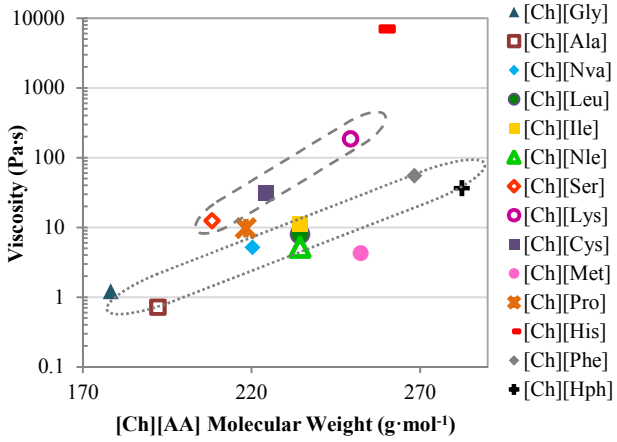

Figure 3.Viscosity of [Ch][AA] ILs at 25 °C as a function of the IL molecular weight. The two domains are used to approximately highlight the trend for AA with only alkyl chains (dotted line) and AA with heteroatoms on the side chain (dashed line).

main groups, the first one characterized by the presence of only alkyl side chains (dotted line) and the other one composed of AA with side chains carrying a heteroatom thus able to form hydrogen bonds (dashed line). As expected [Ch][Ala], [Ch][Nva], [Ch][Leu], [Ch][Ile], [Ch][Nle], [Ch][Phe] and [Ch][Hph] show a linear trend with viscosity increasing with molecular weight, as already obtained for other ILs.[21] This is a consequence of the increase of van der Waals interactions by increasing the length of the alkyl side chain. [Ch][Gly] has higher viscosity than

expected. Indeed, this behaviour has already been observed for other [AA] based ILs[18] and could be due to the higher symmetry of the [Gly] ion with respect to the other [AA] having only alkyl side chains.

The second trend (dashed line) includes the [Ch][AA] ILs carrying heteroatoms ([Ch][Ser], [Ch][Cys] and [Ch][Lys]). Also in this case viscosity increases with molecular weight but the ILs group is shifted of about one order of magnitude to higher viscosity. This is reasonable because of the ability of these AAs to form additional hydrogen bonding interactions with respect to the other group of AAs.[20,22] [Ch][Phe] and [Ch][Hph] are in trend with the first group suggesting that stacking does not contribute significantly to the overall viscosity of the IL. This result will be discussed again taking into account the density data. [Ch][Pro] cannot be uniquely included into any of the two groups. This could be due to its special feature of having the amino group included in a cyclic structure.

[Ch][His] has the higher value of viscosity, well above the values of the other ILs. Going into more details, histidine is well known for its ability to give rise to several types of peculiar interactions in proteins.[23] In particular, it can form strong hydrogen bond interactions with its imidazole group where the polar hydrogen atom of the imidazole is a hydrogen-bond donor, and the basic nitrogen atom is a hydrogen-bond acceptor. Besides, it can also give rise to cation-π interactions with organic cations, in which it acts as the aromatic π-motif in its neutral form. Finally, it can form π-π stacking interactions with itself or other aromatic amino acids and hydrogen-π interactions in which polar hydrogen atoms interacts in a "T" orientation mode with the π-electron density of the aromatic imidazole ring. All of these contributions could be responsible for the very high viscosity value of [Ch][His].The important contribution of strong hydrogen bond of [His] to viscosity is confirmed by our data (not reported in this work) which demonstrate that viscosity decreases abruptly by adding even small amount of water to [Ch][His]. The position of the point representing [Ch][Met] below the series of the ILs with non-polar chains is surprising. Actually, this value can be explained considering the well-known dichotomy of the Met residue.[24,25] In fact, on the one hand, the plot of water accessible surface area of different residues against hydrophobicity puts Met not with completely nonpolar side chains (Ala, Val, Leu and Phe), but with residues containing one dipole such as Ser, Thr, Tyr and His, and the dipole of Met could seem to be rather strong to be a good hydrogen bond acceptor. On the other one, Met residues are not found to be able to form hydrogen bonds thus indicating that divalent sulfur is a poor hydrogen-bond acceptor.[25] This can explain the fact that [Ch][Met] is not in the series of AAs with polar chains. Besides, we can also explain the low value with respect to the AAs series with non-polar chains. In fact, if the increase of viscosity in the non-polar chain AAs series is a consequence of the increase of van der Waals interactions by increasing the length of the alkyl side chain, we should consider that, due to the higher molecular weight of sulfur with respect to carbon, in terms of length of the chains Met should be better compared with Ile, Nle and Leu (four terms side chains). If this correction is made we see that viscosity of [Ch][Met] becomes very similar to those of these three AAs and can be included in the non-polar chain AAs series.

The temperature dependence of viscosity in the range 25-60 °C is reported in Figure 4. It has already been reported that the viscosities of many ionic liquids decrease rapidly upon temperature increase.4 At the highest temperature studied the viscosities decrease at least of one order of magnitude. The semilogarithmic plot is slightly curved which means that the [Ch][AA] ILs do not display an Arrhenius temperature behaviour. Rather, the significant feature of glassy or supercooled liquids is observed. On approaching the glass transition temperature, there is a further increase. This temperature dependence of the viscosity η for glass-forming liquids can be well represented by the Vogel-Fulcher-Tammann (VFT) empirical equation[26] (eq2).

$$\eta = \eta_0 exp\left(\frac{k}{T-T_v}\right) \qquad 2$$

where T is the temperature, η is the viscosity at temperature T, T_v corresponds to the characteristic temperature at which η is infinite, η_0 is a reference viscosity, and k is a constant representing the structural "strength" of the system. The VFT fit curves are shown in Figure 4 and the parameters in the equation are reported in Table 3. The viscosity versus temperature graphs can be well fitted to the VFT model. If compared with the T_g data of [Ch][AA] ILs reported in the literature[10,11](most values are in the range 210-230 K) the values of T_v obtained by the VFT fitting are lower. This behaviour has already been observed by other authors.[27] This is reasonably due to our experimental temperature range (298 - 343 K) which is much higher than the strongly supercooled liquid range. Therefore, although apparently excellent fits to the VFT model are obtained, the T_v values cannot be regarded to be highly accurate.

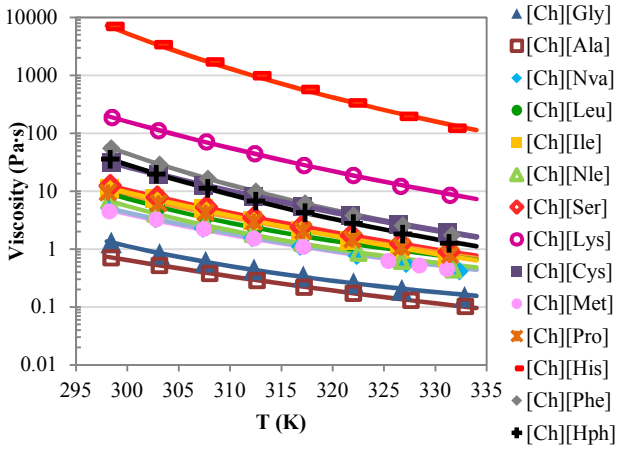

Figure 4 Viscosity as a function of temperature for [Ch][AA] ILs. The lines are the VFT fit curves.

Density measurements

The measured values of densities for all the [Ch][AA] ILs are reported in Table 1. The dependence of the density values on the molecular weight of the AA is reported in Figure 5. Densities range from about 1.05 to 1.20 g·cm^{-3}. As already observed for viscosity data, there is a reasonable agreement of our data with that reported by Tao et al.[11] Understanding the correlation of the density with the structure of the ILs anion is not an easy task. Sometimes density decreases with increasing molecular weight of the anion,4[28-32] in other ILs the opposite behavior is found.4 The

presence of hydrogen bond forming groups can give rise to a significant increase of density.[33] The replacement of a methyl group with a phenyl group does not give rise to a significant increase of density.[33,34-36]

Table 3 Parameters obtained by the VFT fit of the temperature dependence of viscosity of [Ch][AA] ILs.

[Ch][AA]	η_0 (Pa·s)	k (K)	T_v (K)	R	σ_r [(a)]
[Ch][Gly]	$5.48\cdot10^{-03}$	305.89	242.55	0.99951	0.043297
[Ch][Ala]	$1.31\cdot10^{-05}$	1717.60	141.05	0.99996	0.012687
[Ch][Nva]	$1.47\cdot10^{-03}$	681.30	214.55	0.99996	0.062292
[Ch][Leu]	$1.04\cdot10^{-02}$	382.80	241.74	0.99880	0.095817
[Ch][Ile]	$7.31\cdot10^{-06}$	2011.50	157.16	0.99994	0.040639
[Ch][Nle]	$7.23\cdot10^{-03}$	389.44	241.37	0.99988	0.083027
[Ch][Ser]	$3.48\cdot10^{-05}$	1640.90	170.01	0.99986	0.017894
[Ch][Lys]	$2.44\cdot10^{-05}$	2185.10	160.73	0.99989	0.029377
[Ch][Cys]	$6.80\cdot10^{-05}$	1583.50	176.98	0.99998	0.010665
[Ch][Met]	2.4710^{-03}	590.32	220.23	0.99889	0.071268
[Ch][Pro]	$9.91\cdot10^{-06}$	2103.40	145.54	0.99994	0.012550
[Ch][His]	$4.01\cdot10^{-03}$	1280.80	209.09	0.99997	0.070345
[Ch]Phe]	$6.77\cdot10^{-04}$	882.95	220.38	0.99995	0.044904
[Ch][Hph]	$2.4405\cdot10^{-4}$	1031.70	211.64	0.99997	0.034194

[(a)] $\sigma_r = \sqrt{\frac{\sum_i[(\eta_i^{exp}-\eta_i^{cal})/\eta_i^{cal}]^2}{n-v}}$ where n and v are the number of experimental points and adjustable parameters, respectively.

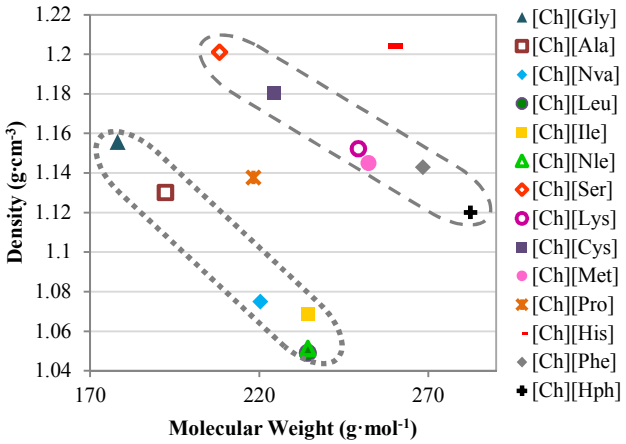

Figure 5 Density of [Ch][AA] ILs at 25 °C as a function of the IL molecular weight. The two domains are used to approximately highlight the trend for AA with only alkyl chains (dotted line) and AA with heteroatoms on the side chain (dashed line).

Often, the situation is simpler with the cations. In particular, for imidazolium based ILs the density usually decreases by increasing the alkyl chain length on the imidazolium cation.[32,37,38] The situation of AA anions could be similar to that of the imidazolium cation since they have different side chains bound to the α carbon. Same as viscosity, data have been grouped into two sets (Figure 5). The influence on density of the length of alkyl chains without heteroatoms can be inferred analyzing data referring to [Ch][Gly], [Ch][Ala], [Ch][Nva], [Ch][Leu], [Ch][Ile] and [Ch][Nle] The density of these ILs decreases with increasing alkyl chain length. Branching effect is not clearly inferable since [Ch][Leu] and [Ch][Nle] show very similar density. In ILs the dispersive interactions increase with chain length, resulting in a nanostructural organization (separation) in polar and nonpolar regions (domains).[39-41]The nonpolar regions are made up of alkyl groups whereas the polar ones contain the cationic head groups and the anions. Usually, the increase of the volume occupied by the hydrophobic methylene groups is higher than the increase of the mass of the IL, resulting in a lower overall density.

The introduction of groups able to form H-bonds ([Ch][Ser], [Ch][Cys], [Ch][Lys]) leads to a significantly increased density, identifying a second set of data having again density decreasing with increasing molecular weight but which is about 0.1 g·cm^{-3} higher than the other data set. This trend is consistent with results from the literature. Himmler et al.[42] and Kolbeck et al.[43] found a higher density for ILs in which hydrophilic ethylene glycol groups are introduced into the alkyl chain. The higher density of the functionalized systems is therefore attributed to the formation of inter- and intramolecular H-bonds. In particular for ILs, the formation of H-bonds between the ether groups and the acidic hydrogen atoms of the imidazolium ring results in a denser packing than for the non-functionalized ILs.[44,45] However, the main contribution to the density of [Ch][Cys], as for [Ch][Met], should come from the presence of the sulfur atom. In fact, considering that the van der Waals volume contribution of the sulfur atom should not be much greater than about 20 % with respect to that of a methylene group while the molecular weight of sulfur is about 128 % higher than that of a methylene group,[46] the presence of sulfur could give an important contribution to the overall density of the ILs. Using the values of the van der Waals volume of free amino acids in solutions,[4748] which show that Met (0.1749 nm^3) is very similar to Ile (0.1754 nm^3) and Leu (0.1787 nm^3), we can calculate that the contribution of the weight of sulfur to Met with respect to the equivalent molecule of Nle should increase the density of [Ch][Met] with respect to [Ch][Nle] of about 0.08 g·cm^{-3}. Subtracting this value to that of [Ch][Met] we obtain a density of about 1.063 g·cm^{-3} which is very close to that of [Ch][Ile] (1.068 g·cm^{-3}). The same considerations can be done for [Ch][Cys], thus we can conclude that the hydrogen bonds, weaker and less frequently occurring with respect to that formed by the classical hydroxyl group,[25]does not seem to give a significant contribution to the density values. It is worthwhile to compare our densities with those obtained for other AA based ILs. For instance, it is interesting to note that also Muhammad et al.[19] found that [EMIM][Pro] density is higher than that expected for its molecular weight in alkyl chain series with respect to [EMIM][Gly] and [EMIM][Ala]. Similar results were also obtained by Tao et al. who observed that in imidazolium based ILs the presence of the cycloalkyl group in place of the n-alkyl group with the same number of carbons leads to an increase in density.[49] This confirms that this AA anion

cannot be considered as a simple AA carrying an alkyl chain. We think that the insertion of the amino group in the ring structure constrains the alkyl portion in such a way that it cannot form well separated hydrophobic domains as observed for alkyl chains.[39-41,50,51] Furthermore, since proline has a secondary amino group that due the electron donating effect of the alkyl group should have a higher negative charge density, it could give rise to stronger interactions.

The density of [Ch][Phe] and [Ch][Hph] is higher compared to its aliphatic analogues. Also this result is in agreement with the data reported by Tao et al. for benzyl substituted imidazolium based ILs.[49] The authors concluded that the density trend could be roughly related to the C/H ratio in the substituents, with density increasing with increasing C/H ratio from n-alkyl, cycloalkyl, to aromatic functionalities. Stacking interactions could also contribute to the packing of the phenyl substituents and, eventually, to their segregation in hydrophobic domains decreasing the density.

As expected, [Ch][His] has the higher value of density due to the hydrogen bonding ability and the increasing C/H ratio.

The temperature dependence of densities is reported in Figure 6. Usually the temperature dependence of density is fitted with the equation $\rho = A_0 + A_1 T$ where A_0 and A_1 are fitting parameters and T is the Kelvin temperature. The fitting parameters obtained for our data are reported in Table 4.

Standard deviations (SD) were always below $1.5 \cdot 10^{-4}$. The values were found to be very close to those of the same [Ch][AA] ILs measured by Tao et al.[11]Our values are only about 15 % lower than those obtained by Muhammad et al.[52] for [EMIM][AA] ILs with the same AA. This means that, as already observed for density data, [Ch] behaves similarly to [EMIM]. Instead, significantly different values ($7\text{-}10 \cdot 10^{-4}$ g·cm^{-3}·K^{-1})were found for BMIM based ionic liquids with fluorinated anions.[53]

Density values as a function of temperature were used to calculate the thermal expansion coefficient (α_p) defined by the equation:

$$\alpha_p = -\frac{1}{\rho}\left(\frac{\delta\rho}{\delta T}\right) = -\frac{A_1}{A_0 + A_1 T} \qquad 3$$

where A_0 and A_1 are the coefficients reported in Table 4 and T is the. The values of α_p obtained for the [Ch][AA] ILs are reported in Table 5. The values ranging from about 4.4 to $5.6 \cdot 10^{-4}$K^{-1}, are comparable with the values reported by Tao et al[11]and fall in the range of the typical values for ILs.[54,55] All of the investigated [Ch][AA] ILs show a weak temperature dependence of α_p for the range explored in our work, the value of averaged relative deviation in α_p being less than 3 %. This behaviour was already observed for imidazolium, pyridinium, phosphonium, and ammonium-based ILs.[11,54,56] Values of α_p found out for [Ch][AA]ILs are considerably lower than those of molecular organic liquids (10^{-3} K^{-1}), but higher than those of classical molten salts ($1\text{-}2 \cdot 10^{-4}$ K^{-1}). When ILs with different alkyl chain length are compared, *i.e.*[Ch][Gly], [Ch][Ala], [Ch][Nva], [Ch][Leu], [Ch][Ile] and [Ch][Nle], those having smaller alkyl chain show less expansion as compared to those having a longer alkyl chain. The large anion size of the IL reduces the electrostatic interactions and facilitates more expansion. On the contrary, the α_p values for ILs with remarkable additional ability to form hydrogen bonds like [Ch][Ser] and [Ch][His] have less expansion with temperature and, thus, lower values of α_p.[57]

The molar volumes (V_m) of the ionic liquids at different temperatures calculated from their molar mass (MW_{IL}) and density with the equation $V_m = MW_{IL}/\rho$, are reported in Table 6. The obtained values are in reasonable agreement with the expected ones estimated by summing the cholinium cation (93.1 cm^3·mol^{-1})[48]and the AA molar volumes[58] measured in solution by other authors. Our experimental data were higher of less than 12%, which is reasonably because the excluded volume was not considered in the calculation. Plotting V_m as a function of the ILs molecular weight (Figure 7), a reasonable linear trend can be observed. The simpler behavior with respect to the density is reasonable since the molar volume is affected mainly by the size of the groups and is not significantly affected by the interactions among them. [Ch][Leu], [Ch][Ile], [Ch][Nle] and [Ch][Nva] show the most significant positive deviation from the trend. As already discussed previously, this could be due to the tendency to give nanostructural organization (separation) in polar and nonpolar regions (domains) when the alkyl side chain grows up[39,41,43] and the nonpolar regions increase and take up more and more space. To partly confirm the peculiarity of [Ch][Leu] and [Ch][Ile] we have to underline that these ILs are highly sensitive to the presence of water and as soon as the anhydrous ILs (water content <0.2 %) are exposed to the atmosphere, they almost instantaneously form solid crystals on their surface . By adding small amount of water (molar fraction of water $\chi_{H2O/IL}$ = 0.048) [Ch][Leu] becomes turbid and remains as it is up to about $\chi_{H2O/IL}$ = 0.350, when the mixture becomes again a clear solution. A similar behaviour was observed for [Ch][Ile]. The molecular volume V_m can also be correlated with the chain length of the functional group bound to the anion or to the cation. It has been demonstrated that the contribution of the methyl groups to the molar volume is independent on the nature of the anion or the cation.[29,59-62]

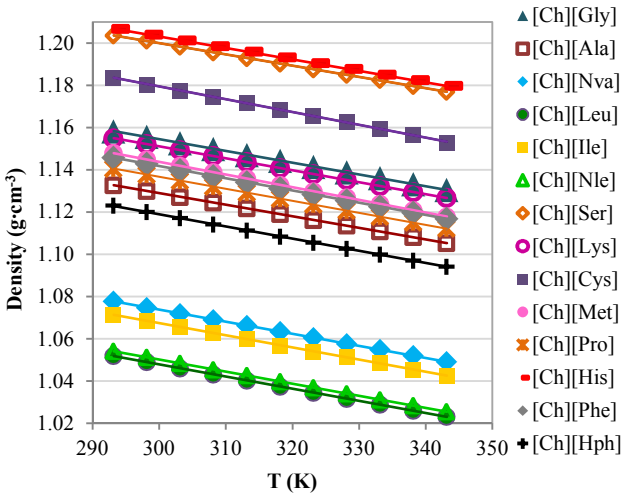

Figure 6 Density as a function of temperature for [Ch][AA] ILs. Lines are linear fits with the equation $\rho = A_0 - A_1 T$.

Table 4 Density parameters obtained by the linear least-squares fit of the data reported in Figure 6 with the equation $\rho = A_0 - A_1 T$.

[Ch][AA]	A_0 (g·cm^{-3})	A_1 (10^{-4}) (g·cm^{-3}·K^{-1})	σ_r(10^4)	R	[Ch][AA]	A_0 (g·cm^{-3})	A_1 (10^{-4}) (g·cm^{-3}·K^{-1})	σ_r(10^4)	R
[Ch][Gly]	1.3211	5.5563	0.73	0.99996	**[Ch][Lys]**	1.3211	5.6656	0.42	0.99999
[Ch][Ala]	1.2931	5.4727	0.49	0.99998	**[Ch][Cys]**	1.3603	6.0287	1.48	0.99987
[Ch][Nva]	1.2448	5.7009	0.53	0.99998	**[Ch][Met]**	1.3242	6.0131	0.40	0.99999
[Ch][Leu]	1.2205	5.7533	0.70	0.99997	**[Ch][Pro]**	1.3069	5.6766	0.25	1.00000
[Ch][Ile]	1.2394	5.7333	0.29	1.00000	**[Ch][His]**	1.3650	5.4007	0.20	1.00000
[Ch][Nle]	1.2219	5.7226	0.37	0.99999	**[Ch][Phe]**	1.3154	5.7858	0.39	0.99999
[Ch][Ser]	1.3595	5.3204	2.67	0.99993	**[Ch][Hph]**	1.29188	5.7640	0.54	0.99998

$\sigma_r = \sqrt{\frac{\sum_i[(\rho_i^{exp} - \rho_i^{cal})/\rho_i^{cal}]^2}{n-v}}$ where n and v are the number of experimental points and adjustable parameters, respectively.

Table 5 Thermal Expansion Coefficient α_p Values of [Ch][AA] ILs as a Function of Temperature.

	α_p (10^{-4} K^{-1})													
T (K)	**[Ch][Gly]**	**[Ch][Ala]**	**[Ch][Nva]**	**[Ch][Leu]**	**[Ch][Ile]**	**[Ch][Nle]**	**[Ch][Ser]**	**[Ch][Lys]**	**[Ch][Cys]**	**[Ch][Met]**	**[Ch][Pro]**	**[Ch][His]**	**[Ch][Phe]**	**[Ch][Hph]**
293.15	4.80	4.83	5.29	5.47	5.35	5.43	4.42	4.91	5.09	5.24	4.98	4.48	5.05	5.13
298.15	4.81	4.84	5.30	5.48	5.37	5.44	4.43	4.92	5.11	5.25	4.99	4.49	5.06	5.15
303.15	4.82	4.86	5.32	5.50	5.38	5.46	4.44	4.93	5.12	5.27	5.00	4.50	5.08	5.16
308.15	4.83	4.87	5.33	5.51	5.39	5.47	4.45	4.94	5.13	5.28	5.01	4.51	5.09	5.17
313.15	4.84	4.88	5.35	5.53	5.41	5.49	4.46	4.95	5.15	5.29	5.03	4.52	5.10	5.19
318.15	4.85	4.89	5.36	5.55	5.42	5.50	4.47	4.97	5.16	5.31	5.04	4.53	5.11	5.20
323.15	4.87	4.90	5.38	5.56	5.44	5.52	4.48	4.98	5.17	5.32	5.05	4.54	5.13	5.21
328.15	4.88	4.91	5.39	5.58	5.45	5.53	4.49	4.99	5.19	5.34	5.07	4.55	5.14	5.23
333.15	4.89	4.93	5.40	5.59	5.47	5.55	4.50	5.00	5.20	5.35	5.08	4.56	5.15	5.24
338.15	4.90	4.94	5.42	5.61	5.48	5.57	4.51	5.02	5.21	5.37	5.09	4.57	5.17	5.25
343.15	4.91	4.95	5.43	5.62	5.50	5.58	4.52	5.03	5.23	5.38	5.10	4.58	5.18	5.27

Table 6 Molar volumes V_m of [Ch][AA] ILs as a Function of Temperature. The numbers close to the IL names are the molecular weights values.

	V_m (cm^3· mol^{-1})													
T (K)	[Ch][Gly] 178.23	[Ch][Ala] 192.26	[Ch][Nva] 220.31	[Ch][Leu] 234.34	[Ch][Ile] 234.34	[Ch][Nle] 234.34	[Ch][Ser] 208.21	[Ch][Lys] 249.35	[Ch][Cys] 224.34	[Ch][Met] 252.37	[Ch][Pro] 218.29	[Ch][His] 258.32	[Ch][Phe] 268.35	[Ch][Hph] 282.35
293.15	153.88	169.74	204.41	222.77	218.73	222.30	173.00	215.91	189.57	219.84	191.39	214.06	234.20	251.42
298.15	154.23	170.14	204.97	223.40	219.33	222.92	173.35	216.40	190.05	220.43	191.87	214.55	234.80	252.09
303.15	154.63	170.58	205.52	224.02	219.92	223.53	173.77	216.94	190.53	221.02	192.35	215.03	235.40	252.75
308.15	155.00	170.99	206.08	224.65	220.52	224.15	174.15	217.49	191.01	221.61	192.84	215.52	236.01	253.41
313.15	155.38	171.41	206.63	225.29	221.11	224.76	174.55	218.03	191.49	222.19	193.32	216.00	236.61	254.06
318.15	155.75	171.81	207.18	225.90	221.71	225.38	174.93	218.57	191.98	222.79	193.81	216.50	237.22	254.73
323.15	156.14	172.25	207.74	226.52	222.31	226.00	175.34	219.12	192.47	223.38	194.30	216.98	237.82	255.39
328.15	156.51	172.66	208.29	227.14	222.92	226.62	175.71	219.66	192.97	223.97	194.79	217.48	238.43	256.05
333.15	156.87	173.09	208.85	227.78	223.53	208.85	176.08	220.21	193.47	224.56	195.28	217.97	239.04	256.72
338.15	157.28	173.52	209.41	228.41	224.14	209.41	176.51	220.76	194.00	225.16	195.78	218.47	239.65	257.38
343.15	157.66	173.95	209.97	229.04	224.75	209.97	176.91	221.31	194.57	225.76	196.28	218.97	240.27	258.05

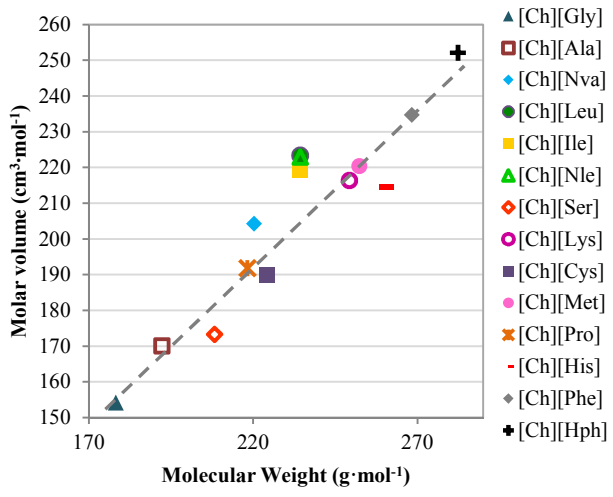

Figure 7 Molar volumes V_m of [Ch][AA] ILs at 25°C as a function of the ILs molecular weight.The dashed line is only a guide for the eye.

For instance, from the slope of the linear fit to dV_m/dn, with n being the chain length of [CnC$_1$Im][Tf2N], the increase of molecular volume per methylene group (–CH$_2$–) was calculated to be 0.0283 nm^3 at 298.15 K, corresponding to a molar volume of 17.0 cm^3·mol^{-1}.[29] These values agree well with the calculations of Glasser et al.(0.0282 nm^3)[60] and Tariq et al. (0.0283 nm^3).[54]

It is not as easy to find a similar correlation for the molar volume of our [Ch][AA] ILs due to the heterogeneity of the AAs structure. In Figure 8 we plotted V$_m$ of [Ch][AA] ILs at 25 °C as a function of the number of –CH$_2$– or CH$_3$ or other functional groups (–CH=, –OH, –SH, –S–, etc.) bound to the alpha carbon of the amino acid. In Figure 8 we can see that it is possible to reasonably fit the data of [Ch][Gly], [Ch][Ala], [Ch][Nva], [Ch][Leu], [Ch][Ile], [Ch][Nle], [Ch][Met] and [Ch][Cys], with a line whose slope results to be 16.3 cm^3 mol^{-1}, corresponding to an increase of molecular volume per functional group of about 0.0271 nm^3. These values are in good agreement with those previously obtained for C$_n$MIM ILs.[29,54,60] The stronger negative deviations from this trend, as expected, were observed for the cyclic systems [Ch][Phe], [Ch][Pro] and [Ch][His] and for the strong hydrogen bond forming [Ch][His], [Ch][Ser] and [Ch][Lys].

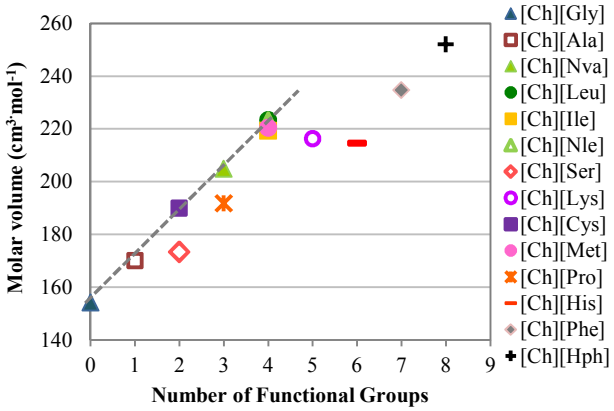

Figure 8 Molar volumes V_m of [Ch][AA] ILs at 25 °C as a function of the of the number of –CH$_2$- or CH$_3$ or other functional groups (-CH=, -

OH, -SH, -S-, etc.) bound to the alpha carbon of the amino acid. The dashed line is a guide to the eye.

Table 7 Experimental and theoretical molar volumes for [Ch][AA] ILs at 25 °C. $\Delta V_m\% = V_m^{exp} - V_m^{cal}$

[Ch][AA]	V_m^{exp}(cm^3· mol^{-1})	V_m^{cal}(cm^3· mol^{-1})	ΔV_m%
[Ch][Gly]	154.23	136.26	11.65
[Ch][Ala]	170.14	153.48	9.79
[Ch][Leu]	222.77	200.68	9.92
[Ch][Ile]	220.43	198.69	9.86
[Ch][Ser]	173.35	153.72	11.32
[Ch][Lys]	216.40	195.62	9.60
[Ch][Met]	219.33	198.39	9.55
[Ch][Pro]	191.87	175.69	8.43
[Ch][His]	214.06	191.77	10.41
[Ch][Phe]	234.80	214.88	8.48

In addition, [Ch][Lys] has a peculiar structure in which a NH_2 group, able to form hydrogen bonds, is present at the end of a long CH_2 chain: this particular structure could undergo some sort of folding of the alkyl chain bringing the NH_2 group in the proximity of the polar domain of the IL (intramolecular hydrogen bonding or hydrogen bonding with the cation)[40,50,51,63] thus creating a situation that could be similar to that of Proline or, in general, of the other cyclic systems.

Refractive Index.

The refractive indices (n_D) measured at 25 °C are listed in Table 1 and the temperature dependence is reported in Figure 9. As seen from the experimental results, the refractive indices decrease linearly with the temperature. n_D values are in the range 1.48-1.54, which demonstrates that there is not a strong influence of the amino acid anion structure on the n_D value. Our values are slightly lower than those measured by Tao et al.[11] for the same [Ch][AA] ILs and are quite similar to those measured by Muhammad et al.[19] for ILs formed by EMIM and the same AA. In general the values are high with respect to many other ILs[64] but, for example, are similar to those measured for nitrile functionalized alkylimidazolium bromide ionic liquids.[65] This could be due to a relatively high electron mobility (high polarizability) around the choline cation and the amino acid anion.

The order of magnitude of the refractive indices is not closely related to the order of anionic molecular weight. Seki et al. demonstrated that the refractive index depends on the molecular polarizability of the ion pairs per molar volume on the basis of the Lorentz−Lorenz equation.[66] This relationship could not be applied to our data (Figure S13). From data reported in Table 1 and Figure S13 it can be seen that the lowest values are observed for the [Ch][AA] ILs with the AA having only a hydrocarburic aliphatic side chain (Ala, Nva, Ile, Nle and Leu) while the highest values are observed for the aromatic AA (Phe, Hph and His). Within the aliphatic series n_D decreases with increasing the side chain length. This behaviour has been observed by other authors,[65] but the opposite dependence has also been reported.[54] In our opinion, as already reported by other authors, this results reinforces the recommendation not to generalize the use of refractive index data to explain at a molecular level the macroscopic behaviour of ionic liquids.[54]

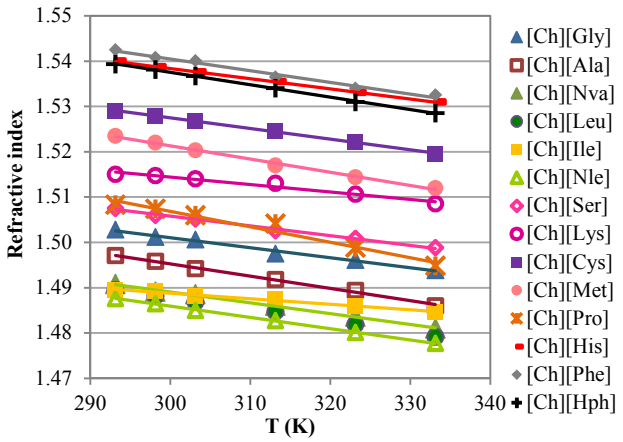

Figure 9 Refractive indices n_D of [Ch][AA] ILs as a function of temperature. Lines are linear fits with the equation $n_D = A_2 - A_3T$ (5).

Conductivity.

The conductivities (σ) of the [Ch][AA] ILs at 25 °C were between 0.12 and 90.6 μS·cm^{-1} (Table 1). The values are similar to those reported by Tao et al. for five [Ch][AA] ILs,[67] except for [Ch][Pro] which have a σ value more than an order of magnitude higher. Conductivity is mainly dependent on the number and mobility of charge carriers. The relatively low conductivities of the [Ch][AA] ILs is maybe due to the low mobility of the charge carriers, which is caused by the strong contribution of hydrogen bonding interactions. [Ch][AA] ILs conductivities at 25 °C show a good linear correlation with viscosity in a double logarithmic plot (Figure 10). In the case of amino functionalised phosphonium-based ionic liquids [aP4443][AA] ILs the authors found that the conductivities at 25 °C are mainly governed by the mobility of the charge carriers.[20] It is interesting to note that conductivities at 25 °C for relatively low viscous [Ch][AA] ILs ([Ch][Gly], [Ch][Ala]) are close to those of the corresponding [aP4443][AA] ILs. Conductivities of the other [Ch][AA] ILs decrease dramatically as a consequence of the increase of viscosity which for some of them is of 2-3 orders of magnitude. On the contrary, viscosities of [aP4443][AA] ILs does not increase more than one order of magnitude and, consequently, σ values change much less than for [Ch][AA] ILs.

Conductivity measurements were also performed over the temperature range 293.15 - 363.15 K (Figure 11). It can be seen that the temperature dependence is more pronounced for the ILs with the lower conductivities, reflecting mainly the variation of

the viscosity with the temperature (Figure 4). The temperature dependence could be well described by the VTF type equation:

$$\sigma\ (\mu S \cdot cm^{-1}) = A_4 exp\left(\frac{-A_5}{T-A_6}\right) \quad 5$$

where A_4, A_5, and A_6 are correlation coefficients estimated using linear regression analysis. The coefficients values together with the standard deviations are reported in Supporting Info. The experimental data are very well fitted by the VFT equation (Figure 11).

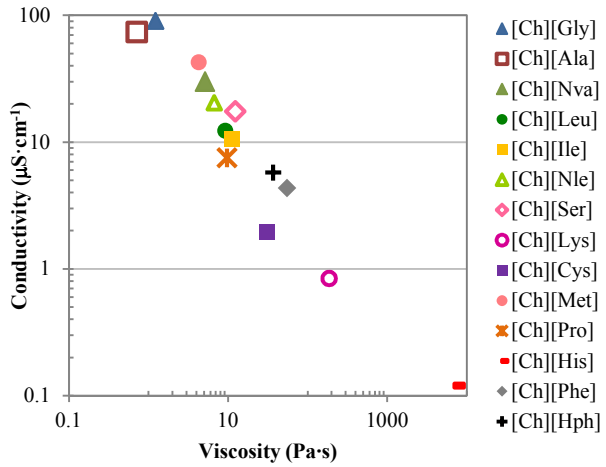

Figure 10 Conductivity σ of [Ch][AA] ILs as a function of viscosity at 25 °C.

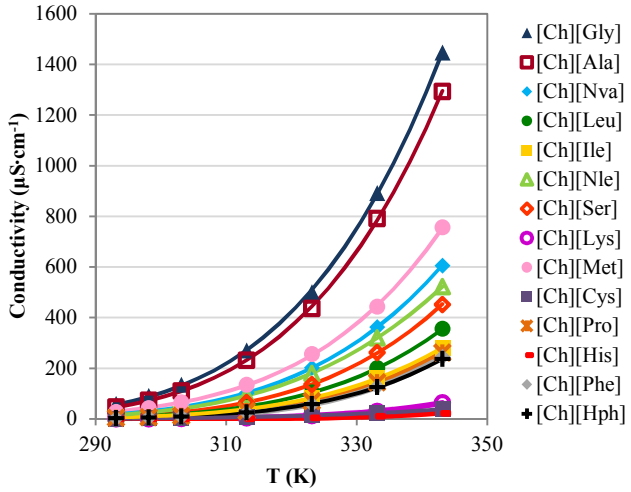

Figure 11 Conductivity σ of [Ch][AA] ILs as a function of temperature. Curve fits are obtained with equation 4.

Conclusions

[Ch][AA] RTILs were obtained with a new synthesis method based on a potentiometric titration. This method provides several advantages like shorter preparation time, no use of organic solvents, yields close to 100%, high reproducibility, thus resulting significantly more environmentally friendly. We obtained 14 out of the 18 possible [Ch][AA] ILs tested; none of the potential dianionic $[Ch]_2[AA]$ salts with amino acids having two ionisable groups resulted in a RTIL. Physico-chemical properties, such as density, viscosity and conductivity were demonstrated to be well correlated with the structural features of the amino acids. Densities values were comparable with those of similar ILs. Viscosity values ranges in a wide interval reaching extremely high values ([Ch][His]). Conductivities are relatively low and depend strongly on the viscosity. Empirical equations well fitted the temperature dependence of these parameters in a wide temperature range. The values were compared with the data already reported in literature for some [Ch][AA] ILs. The thermal expansion coefficient α_p and the molar volume V_m values were also calculated from the acquired experimental density values. Due to the high number of AAs explored and to their structural heterogeneity we have been able to find some interesting correlations between the data obtained and the structural feature of the AAs in terms of alkyl chain length, hydrogen bonding ability, stacking and cyclization.

Acknowledgments

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† Electronic Supplementary Information (ESI) available: [^{1}H NMR spectra]. See DOI: 10.1039/b000000x/

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