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Synthesis and Thermophysical Properties of Biocompatible Cholinium-Based Amino Acid Ionic Liquids

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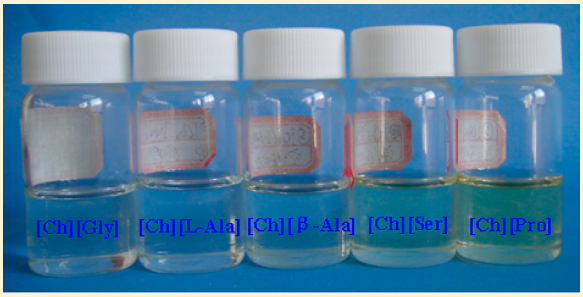
Supporting Information

ABSTRACT: Nowadays the knowledge of thermodynamic properties for amino acid ionic liquids (AAILs) has been paramount for the design of many chemical processes. In this present work, a series of cholinium-based AAILs ([Ch][AA]) were synthesized by neutralization of choline hydroxide solution with five amino acids and then were characterized by ^{1}H NMR, Fourier transform infrared (FT-IR), elemental analysis, thermogravimetry, and differential scanning calorimetry (DSC) analysis. Physico-chemical properties such as density, viscosity, refractive index, and conductivity were measured and correlated with the empirical equations in a wide temperature range. The thermal expansion coefficient values were also calculated from the acquired experimental density values. From the experimental data, it was found that the density, viscosity, and refractive index decreased while conductivity increased with the increase of temperature. The correlation results were proposed to be in good agreement with the experimental data, and optimal fitting parameters were presented. In addition, the coefficient of thermal expansion was considered to be independent of temperature in the range of (298.15 to 353.15) K.



INTRODUCTION

Ionic liquids (ILs) have been attracting more attention in recent years due to their excellent characteristics: low vapor pressure, nonflammability, high thermal and chemical stability, outstanding solubility, and possibility of recycling.[1−3] Based on these properties, ILs have emerged as a novel class of compounds to be used in many fields such as electrochemistry, organic synthesis, catalysis, gas separation, and so on. However, among a large number of ILs that had been synthesized and characterized, the traditional imidazolium- and pyridinium-based ILs had been demonstrated to be badly biodegradable and poorly biocompatible. Some of these ILs carrying long alkyl side-chains increased their toxicities considerably.[4,5] In addition, the feedstocks used to produce these ILs were of nonrenewable petroleum origin. To overcome the above-mentioned drawbacks, the study of nontoxic and environmentally benign ILs from renewable materials therefore has been highly conceived and proposed, thus meeting with one of the main principles of green chemistry.[6]

Amino acids, as one of the most abundant biomaterials in nature, are known to be nontoxic, biodegradable, and biocompatible. They are excellent feedstocks for the synthesis of ILs, owing to their reasonable cost and environment-friendly characteristics. In 2005, a group of amino acid ionic liquids (AAILs) was first synthesized by Fukumoto's group from 20 natural amino acids.[7] Since then, many ILs in which the forming anion comes from a natural product had been prepared.[8−11] In addition, choline, another green natural product, is an essential micronutrient for normal functioning of all cells. Recently, several cholinium-based ILs had been synthesized and characterized.[12−15] The majority of cholinium-based ILs were reported to be readily biodegradable and lowly toxic, owing to its cholinium cation containing a hydroxyl group.[16] For example, Elliott and Weaver had synthesized five choline phosphate ILs and observed that these cholinium ILs exhibited excellent biocompatibility and biodegradability.[14] The anion size and the presence of moderately long and/or branched alkyl chains were considered to be major factors to affect cell viability. Pereira and Petkovic had further prepared several cholinium ILs combined with a range of alkanoate anions and found that the cholinium alkanoate ILs showed good biocompatibility and low toxicity to filamentous fungi.[15] Therefore, it is a very attractive proposal that biocompatible cholinium-based AAILs ([Ch][AA]) can be designed and synthesized by using choline chloride ([Ch]Cl) as the source for the cation and amino acids for the different anions. These [Ch][AA] ILs could provide a variety of applications, such as functional materials, gas absorption, and green catalysis in the fields of industrial and pharmaceutical chemistry.

In 2010, Calvino-Casilda and co-workers reported their early work on the synthesis of [Ch][AA], and these AAILs were successfully applied as catalysts for the Knoevenagel condensation reactions between benzaldehyde and different active methylene compounds with high conversion and selectivity.[17]

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After that, Zong et al. had further explored the properties of [Ch][AA] ILs and found that the selective extraction of lignin from lignocellulose was enhanced significantly using the [Ch][Gly] ILs as a solvent.[18] Therefore, to study the potential of such AAILs to be applied in various fields of chemical industry, the physicochemical properties of AAILs are very important for analysis. Even though a great number of research groups are working on this subject and the number of published papers on physical properties of AAILs has increased exponentially during the past decade, the effect of temperature and anion size on the physicochemical properties of [Ch][AA] ILs has not been studied systematically yet. It is very worth noting that to date the properties of such AAILs remain unknown.

In this work, five AAILs, cholinium glycinate ([Ch][Gly]), cholinium L-alaninate ([Ch][L-Ala]), cholinium β-alaninate ([Ch][β-Ala]), cholinium prolinate ([Ch][Pro]), and cholinium serinate ([Ch][Ser]), were synthesized from choline hydroxide and amino acids via simple neutralization reactions. The general synthetic route of the [Ch][AA] ILs was depicted in Figure 1, and they were characterized by NMR spectroscopy,

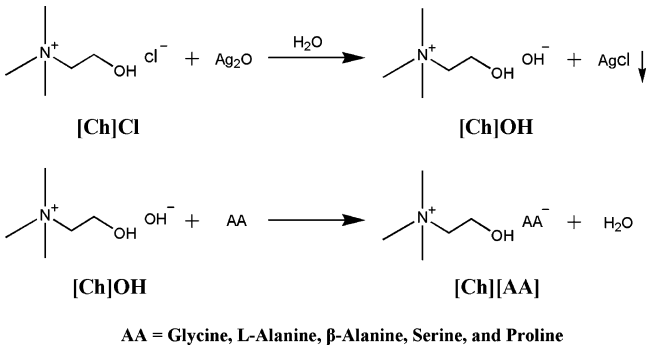

Figure 1. General route for the synthesis of [Ch][AA] ILs.

Fourier transform infrared (FT-IR) spectroscopy, elemental analysis, thermogravimetry, and differential scanning calorimetry (DSC) analysis. Some key physical properties (density, viscosity, refractive index, and conductivity) have been measured as a function of temperature at atmosphere pressure, while the influence of anion size on those properties was also discussed.

EXPERIMENTAL SECTION

Materials. The glycine (purity ≥ 99 %), L-alanine (purity ≥ 99 %), β-alanine (purity ≥ 99 %), L-serine (purity ≥ 99 %), L-proline (purity ≥ 99 %), and choline chloride (purity ≥ 99 %) were purchased from Aladdin Chemical Reagent Co. Ltd. (Shanghai, China). Silver oxide and ethanol were of analytical grade and used without any further purification. Doubly distilled water was used in all experiments.

Preparation and Characterization of [Ch][AA] ILs. Five AAILs, [Ch][Gly], [Ch][L-Ala], [Ch][β-Ala], [Ch][Ser], and [Ch][Pro], were synthesized by the procedure as follows (Figure 1). In the first step, [Ch]OH aqueous solution was obtained from the metathesis of [Ch]Cl (0.05 mol) with Ag_2O (0.025 mol) by using water as the solvent. In the second step, it was centrifuged and filtered; [Ch]OH containing filtrate was then neutralized with an equimolar aqueous solution of amino acid by stirring at room temperature for 12 h. After neutralization, water was evaporated under vacuum at 323.15 K. The excess amino acid was precipitated by adding ethanol. After filtration the AAIL was in a vacuum oven containing P_2O_5 at 363.15 K for 48 h to remove the residual water prior to use. Five [Ch][AA] ILs were then obtained with the yields of more than 80 % (on the base of [Ch]Cl), though it consumed too much time for synthesis. Thus, the structures of [Ch][AA] ILs were confirmed by ^{1}H NMR, elemental analysis, and FT-IR spectra (available as Supporting Information) and are in good agreement with the literature.[17] Then the purities of these AAILs were estimated to be greater than 99 % (mass fraction) from ^{1}H NMR and elemental analysis. In addition, the water content was less than 150 ppm in all of these [Ch][AA] ILs, which was analyzed by Karl Fischer titration (Metrohm 756 KF coulometer). The concentration of Cl^- in each [Ch][AA] IL was measured by Mohr titration, and the related impurity was less than 0.02 wt %. The [Ch][AA] ILs also had a calculated Ag^+ concentration of parts per billion level from the limited solubility product of AgCl.

Physical Properties. Before measuring the properties such as density, viscosity, refractive index, conductivity, and thermal stability, all of the [Ch][AA] ILs were drying in vacuum at 353.15 K. All instruments used for physical property measurements were calibrated using Millipore-quality water as described elsewhere.[19,20] An Anton Paar densimeter (model DMA4500) and cone−plate viscometer (Brookfield DV II+ Pro) were used to measure the densities and viscosities, respectively, over the temperature range (298.15 to 353.15) K with a temperature control of ± 0.05 K. The precision of the density apparatus was ± 0.001 g·cm^{-3}, which was also calibrated with dry air before each series of measurements. The attaining thermal equilibrium time in the viscometer was about 30 min, and the uncertainties were estimated to be ± 5.5 %. Refractive indices were determined at temperatures from (293.15 to 343.15) K using a Rudolph research analytical J357 refractometer with a measuring accuracy of ± 0.001 and a temperature precision of ± 0.05 K. The apparatus was calibrated before each series of measurements and checked using pure organic solvents with known refractive index.[21] Conductivity was determined by a conductivity meter (DDJS-308A, Shanghai Leici Company) with a DJS-1C electrode. Caution was taken to prevent evaporation, and the electrode and the solution were sealed in typical glassware, which was immersed into a thermostatic bath with an accuracy of ± 0.05 K. The uncertainty of the conductivity data was ± 3 %. In addition, the optical rotations, $[\alpha]_D^{20}$, for the three chiral ILs ([Ch][L-Ala], [Ch][Ser], and [Ch][Pro]) were also measured in aqueous solution (c = 2) using an automatic indication polarimeter (Atago-AP300) with a measuring accuracy of ± 0.03.

Thermal Properties. The thermal stability of [Ch][AA] ILs and [Ch]Cl was determined by a PerkinElmer Diamond TG/DTA thermal gravimetric analyzer. The samples were placed in an aluminum pan under nitrogen atmosphere at a heating rate of 10 °C·min^{-1} with temperature accuracy better than ± 3 °C. The decomposition temperatures (T_d) were then taken as the onset of mass loss, defined as the intersection of the baseline before decomposition and the tangent to the mass loss afterward. Further, the glass transition temperatures (T_g) of these [Ch][AA] ILs were determined with a differential thermal analyzer (Netzsch DSC 200F3) with a heating rate of 10 °C·min^{-1}, after cooling samples to −80 °C under nitrogen. The DSC instrument was calibrated by the standard reference indium and zinc sample, and the uncertainty was ± 0.1 °C.

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RESULTS AND DISCUSSION

Density. The densities of all five AAILs measured in the temperature range from (298.15 to 353.15) K and atmospheric pressure are presented in Table 1 and plotted as a function of T

Table 1. Experimental Density Values, ρ, at Temperature T, for [Ch][AA] ILs at Pressure p = 0.1 MPa[a]

	ρ/(g·cm^{-3})				
T/K	[Ch][Gly]	[Ch][L-Ala]	[Ch][β-Ala]	[Ch][Pro]	[Ch][Ser]
298.15	1.14520	1.11294	1.12029	1.12104	1.19151
303.15	1.14231	1.11007	1.11751	1.11821	1.18865
308.15	1.13943	1.10701	1.11455	1.11535	1.18579
313.15	1.13670	1.10404	1.11177	1.11249	1.18290
318.15	1.13397	1.10121	1.10898	1.10961	1.17992
323.15	1.13122	1.09837	1.10620	1.10669	1.17687
328.15	1.12846	1.09554	1.10343	1.10368	1.17397
333.15	1.12570	1.09269	1.10063	1.10061	1.17120
338.15	1.12293	1.08985	1.09783	1.09781	1.16838
343.15	1.12022	1.08704	1.09504	1.09503	1.16550
348.15	1.11753	1.08427	1.09232	1.09212	1.16254
353.15	1.11483	1.08151	1.08960	1.08939	1.15937

[a]Standard uncertainties u are $u(T)$ = 0.05 K and $u(p)$ = 10 kPa, and the combined expanded uncertainty U_c is $U_c(\rho)$ = 0.001 g·cm^{-3} with a 0.95 level of confidence ($k \approx 2$).

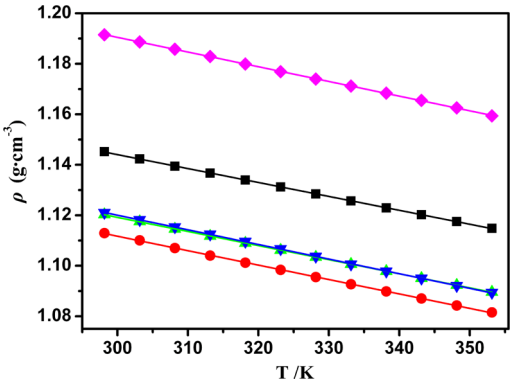

Figure 2. Densities ρ as a function of temperature: ■, [Ch][Gly]; red ●, [Ch][L-Ala]; green ▲, [Ch][β-Ala]; blue ▼, [Ch][Pro]; pink ◆, [Ch][Ser].

in Figure 2. It was observed that the densities of these present AAILs decreased linearly with increasing temperature, and the density order was as follows: [Ch][L-Ala] < [Ch][β-Ala] ≈ [Ch][Pro] < [Ch][Gly] < [Ch][Ser]. Thus, these results show that the temperature has an inverse effect on density, and an increase in the anion molecular weight does not directly correspond to the rise in the density values for the present AAILs. The hydrogen bonding interaction existed in [Ch][Gly] and [Ch][Ser] is considered to be the main reason to result in higher densities, even though the molecular mass of the anions of these two AAILs are relatively small. A similar behavior for other AAILs and imidazolium-based ILs was also observed by Muhammad et al.[21] and Gardas et al.[22]

Viscosity. The experimental data of the viscosities are given in Table 2, and Figure 3 shows the effect of temperature on viscosities of AAILs in the temperature range of (298.15 to 353.15) K. It was indicated that the structures of anions had a

Table 2. Experimental Dynamic Viscosity Values, η, at Temperature T, for [Ch][AA] ILs at Pressure p = 0.1 MPa[a]

	η/(mPa·s)				
T/K	[Ch][Gly]	[Ch][L-Ala]	[Ch][β-Ala]	[Ch][Pro]	[Ch][Ser]
298.15	182.3	385.6	5092.1	10643.8	11543.7
303.15	119.9	234.9	3022.2	5437.3	6543.1
308.15	84.3	136.8	1820.4	2824.6	3793.3
313.15	50.2	89.0	1146.2	1515.3	2186.5
318.15	29.4	51.8	723.2	839.1	1306.0
323.15	19.9	31.5	470.7	463.5	811.5
328.15	14.3	21.5	322.4	307.0	522.9
333.15	10.4	14.0	220.7	163.7	346.6
338.15	7.2	10.0	155.9	114.0	237.7
343.15	5.5	7.4	112.0	70.1	167.5
348.15	4.3	5.7	79.3	46.3	120.1
353.15	3.5	4.4	56.7	33.7	90.2

[a]Standard uncertainties u are $u(T)$ = 0.05 K and $u(p)$ = 10 kPa, and the combined expanded uncertainty U_c is $U_c(\eta)$ = 5.5 % with a 0.95 level of confidence ($k \approx 2$).

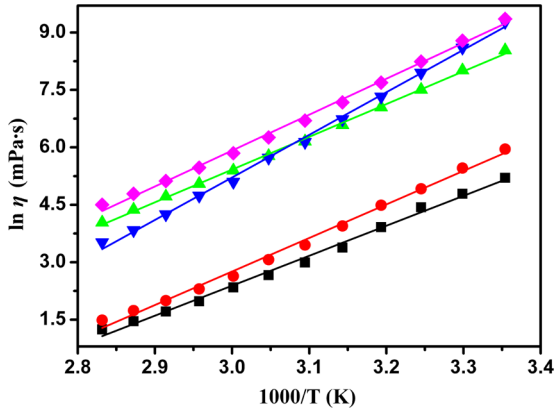

Figure 3. Viscosities η as a function of temperature: ■, [Ch][Gly]; red ●, [Ch][L-Ala]; green ▲, [Ch][β-Ala]; blue ▼, [Ch][Pro]; pink ◆, [Ch][Ser].

significant effect on the viscosities of [Ch][AA] ILs. An increase in the size of the anion generally resulted in a higher viscosity, which might be ascribed to stronger van der Waals and/or hydrogen bond interactions.[13,21,23] For example, the [Ch][Gly] IL, with the simplest amino acid anion, displayed the lowest viscosity. The [Ch][Ser] IL performed a large viscosity due to the introduction of hydroxyl group (11543 mPa·s) accompany with strong hydrogen bond interactions.

Refractive Index. The measured data of the refractive indices of the above synthesized [Ch][AA] ILs are presented in Table 3, and the effect of temperature on refractive index is also given in Figure 4. As seen from the experimental results, the refractive index was found to be linearly decreasing with an increase in temperature, and the order was [Ch][L-Ala] < [Ch][Gly] < [Ch][β-Ala] < [Ch][Pro] < [Ch][Ser]. Thus, it had been noted that the refractive indexes were clearly dependent on the anionic structure. For example, [Ch][L-Ala] was of the lowest refractive index due to the small size in the [L-Ala]$^-$ anion. The higher refractive index values of [Ch][Ser] ILs could be ascribed to the extra electron mobility around the additional OH group in [Ser]$^-$ anion. This was also in good agreement with that reported by Muhammad et al.[21] for other imidazolium AAILs.

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Table 3. Experimental Refractive Index Values, n_D, at Temperature T, for [Ch][AA] ILs at Pressure p = 0.1 MPa[a]

	n_D				
T/K	[Ch][Gly]	[Ch][L-Ala]	[Ch][β-Ala]	[Ch][Pro]	[Ch][Ser]
293.15	1.5238	1.5146	1.5322	1.5419	1.5447
298.15	1.5224	1.5140	1.5313	1.5408	1.5429
303.15	1.5213	1.5127	1.5306	1.5402	1.5416
308.15	1.5204	1.5118	1.5294	1.5390	1.5408
313.15	1.5194	1.5105	1.5285	1.5379	1.5397
318.15	1.5182	1.5094	1.5277	1.5367	1.5388
323.15	1.5171	1.5084	1.5266	1.5355	1.5382
328.15	1.5158	1.5072	1.5260	1.5344	1.5366
333.15	1.5148	1.5060	1.5249	1.5329	1.5349
338.15	1.5137	1.5052	1.5238	1.5317	1.5341
343.15	1.5125	1.5041	1.5225	1.5306	1.5326

[a]Standard uncertainties u are $u(T)$ = 0.05 K and $u(p)$ = 10 kPa, and the combined expanded uncertainty U_c is $U_c(n_D)$ = 0.001 with a 0.95 level of confidence ($k \approx 2$).

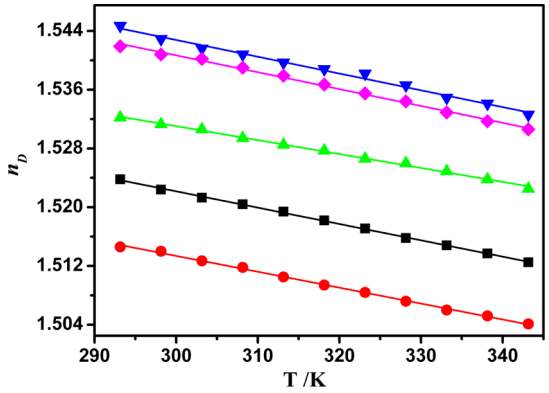

Figure 4. Refractive index n_D as a function of temperature: ■, [Ch][Gly]; red ●, [Ch][L-Ala]; green ▲, [Ch][β-Ala]; pink ◆, [Ch][Pro]; blue ▼, [Ch][Ser].

Conductivity. Conductivity measurements were performed over the temperature range (298.15 to 353.15) K. The experimental data were listed in Table 4, and the effect of temperature on the conductivity was also illustrated in Figure 5.

Table 4. Experimental Conductivity Values, σ, at Temperature T, for [Ch][AA] ILs at Pressure p = 0.1 MPa[a]

	$\sigma/(\mu s \cdot cm^{-1})$				
T/K	[Ch][Gly]	[Ch][L-Ala]	[Ch][β-Ala]	[Ch][Pro]	[Ch][Ser]
298.15	67.7	21.3	7.1	0.3	9.3
303.15	104.0	57.7	14.3	1.3	14.5
308.15	146.8	90.7	26.8	3.5	22.9
313.15	220.3	125.5	49.4	7.0	35.9
318.15	292.1	170.4	90.7	13.0	55.3
323.15	388.2	249.3	133.6	20.4	83.3
328.15	496.7	309.3	177.8	29.1	121.7
333.15	609.3	397.3	227.2	43.5	174.9
338.15	781.3	518.1	295.5	55.2	266.4
343.15	992.7	655.5	379.1	64.9	370.3
348.15	1218.7	822.3	496.2	77.9	495.4
353.15	1499.4	1006.3	615.4	94.1	688.1

[a]Standard uncertainties u are $u(T)$ = 0.05 K and $u(p)$ = 10 kPa, and the combined expanded uncertainty U_c is $U_c(\sigma)$ = 3 % with a 0.95 level of confidence ($k \approx 2$).

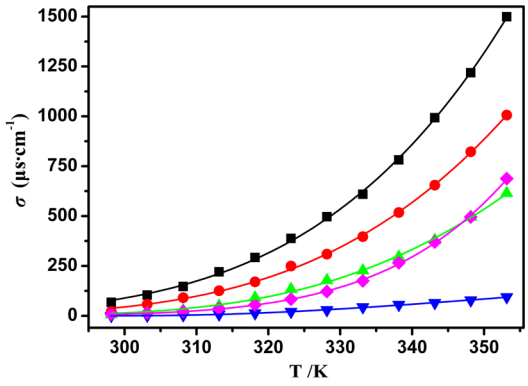

Figure 5. Conductivity σ as a function of temperature: ■, [Ch][Gly]; red ●, [Ch][L-Ala]; green ▲, [Ch][β-Ala]; blue ▼, [Ch][Pro]; pink ◆, [Ch][Ser].

It was demonstrated that the conductivity increased with increasing temperature. As expected, the conductivity decreased with the increase of the anion molecular size of [Ch][AA] ILs, a contrario of the viscosity.[24] In light of this observation, the mobility decreased with increasing of the van der Waals forces. For example, at 303.15 K the conductivity decreased up to seven times by changing the $[Ser]^-$ anion instead of the $[Gly]^-$ anion combined with the $[Ch]^+$ cation. Additionally, by increasing the temperature from (303.15 to 343.15) K, the conductivity increased up to around 10 times in the case of [Ch][Gly].

On the basis of the above observations, the investigated physical properties for the present [Ch][AA] ILs were fitted to the following empirical equations as a function of temperature.[21,24−26]

$$\rho/(g \cdot cm^{-3}) = A_1 + A_2 T \quad (1)$$

$$\ln \eta/(mPa \cdot s) = A_3 + A_4/T \quad (2)$$

$$n_D = A_5 + A_6 T \quad (3)$$

$$\sigma/(\mu s \cdot cm^{-1}) = A_7 \exp\left(\frac{-A_8}{T - A_9}\right) \quad (4)$$

where ρ, η, n_D, and σ denote are the density, viscosity, refractive index, and conductivity, respectively. A_1, A_2, A_3, A_4, A_5, A_6, A_7, A_8, and A_9 are correlation coefficients. T is the Kelvin temperature. The correlation coefficients were estimated using linear regression analysis, and the values were reported together with the standard deviations (SD) in Tables 5, 6, 7, and 8. The SD values were calculated by using the following expression:

Table 5. Fitting Parameter Values of eq 1 and the Standard Deviations (SDs)

ILs	A_1	$A_2 \cdot 10^4$	SD·10^4	R^2
[Ch][Gly]	1.30932	−5.51035·	0.81345	0.99997
[Ch][L-Ala]	1.28311	−5.71371	1.27076	0.99993
[Ch][β-Ala]	1.28666	−5.58315	0.68802	0.99998
[Ch][Pro]	1.29387	−5.79448	1.05357	0.99995
[Ch][Ser]	1.36507	−5.81972	1.05781	0.99995

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Table 6. Fitting Parameter Values of eq 2 and the Standard Deviations (SDs)

ILs	A_3	$A_4 \cdot 10^3$	SD	R^2
[Ch][Gly]	−21.08588	7.8244	0.10557	0.99718
[Ch][L-Ala]	−23.51817	8.7588	0.11254	0.99744
[Ch][β-Ala]	−20.22579	8.5486	0.05449	0.99937
[Ch][Pro]	−28.12994	11.1150	0.09649	0.99883
[Ch][Ser]	−22.20434	9.3736	0.09479	0.99841

Table 7. Fitting Parameter Values of eq 3 and the Standard Deviations (SDs)

ILs	A_5	$A_6 \cdot 10^4$	SD·10^4	R^2
[Ch][Gly]	1.58887	−2.2236	1.18535	0.99954
[Ch][L-Ala]	1.57834	−2.1654	1.54364	0.99917
[Ch][β-Ala]	1.58792	−1.8964	1.86705	0.99842
[Ch][Pro]	1.60963	−2.2982	2.50333	0.99806
[Ch][Ser]	1.61134	−2.2855	3.71334	0.99571

Table 8. Fitting Parameter Values of eq 4 and the Standard Deviations (SDs)

ILs	A_7	A_8	A_9	R^2
[Ch][Gly]	$5.0909 \cdot 10^6$	1678.529	146.763	0.99959
[Ch][L-Ala]	$8.1431 \cdot 10^5$	1121.363	185.691	0.99941
[Ch][β-Ala]	$1.4459 \cdot 10^5$	716.418	222.067	0.99852
[Ch][Pro]	$8.0515 \cdot 10^2$	158.621	279.647	0.99869
[Ch][Ser]	$8.8265 \cdot 10^7$	2320.466	155.952	0.99959

$$SD = \sqrt{\frac{\sum_i^N (Z_{exp} - Z_{calc})^2}{N}} \quad (5)$$

where N is the number of experimental points and Z_{exp} and Z_{cal} are the experimental and calculated values (using eqs 1, 2, 3, and 4), respectively.

As seen from Tables 5, 6, 7, and 8, it was noted that all of the correlation coefficients were over 0.99. The temperature dependence of viscosity and conductivity could be well-described by the Arrhenius and Vogel−Tamman−Fulcher (VTF) equations. The values of the parameters of density and refractive index for the [Ch][AA] ILs were also found to be close to those of the choline carboxylate ILs obtained by Mohanad and Yin,[27] due to the same cation $[Ch]^+$ in these two classes of ILs. Moreover, according to eq 4, if the IL owned the bigger A_9 value, the IL conductivity was more insensitive with temperature changing over the studied temperature range. For example, Table 8 showed that the [Ch][Pro] IL had the maximum A_9 value, and the conductivity data as investigated in Table 4 demonstrated that the values of the conductivity of [Ch][Pro] IL changed very little in the temperature range of (298.15 to 353.15) K.

In addition, since the temperature−density relationship for these [Ch][AA] ILs was linear, density values as a function of temperature were used to calculate the thermal expansion coefficient (α_p) (Table 9). The thermal expansion coefficients (α_p), also known as volume expansivity, as a function of temperature at atmospheric pressure were determined by using the following eq 6:

$$\alpha = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_P = -\frac{A_2}{A_1 + A_2 T} \quad (6)$$

Table 9. Thermal Expansion Coefficient Values of [Ch][AA] ILs as a Function of Temperature

	$\alpha_p \cdot 10^4/(K^{-1})$				
T/K	[Ch][Gly]	[Ch][L-Ala]	[Ch][β-Ala]	[Ch][Pro]	[Ch][Ser]
298.15	4.81	5.13	4.98	5.17	4.88
303.15	4.82	5.15	4.99	5.18	4.90
308.15	4.83	5.16	5.01	5.19	4.91
313.15	4.85	5.17	5.02	5.21	4.92
318.15	4.86	5.19	5.03	5.22	4.93
323.15	4.87	5.20	5.05	5.24	4.94
328.15	4.88	5.21	5.06	5.25	4.96
333.15	4.89	5.23	5.07	5.26	4.97
338.15	4.90	5.24	5.08	5.28	4.98
343.15	4.92	5.26	5.10	5.29	4.99
348.15	4.93	5.27	5.11	5.31	5.01
353.15	4.94	5.28	5.12	5.32	5.02

where α_p, ρ, and T are the thermal expansion coefficient, density, and absolute temperature, respectively, whereas A_1 and A_2 are the fitting parameters of eq 1. As seen from Table 9, it was observed that the values of thermal expansion coefficient did not appreciably change with temperature for the range from (298.15 to 353.15) K. The value of averaged relative deviation in α_p was found to be less than 3 %. Thus, it was demonstrated that the thermal expansion coefficient of [Ch][AA] ILs was almost independent of temperature, and this phenomenon was also observed similar to those reported for imidazolium, pyridinium, phosphonium, and ammonium-based ILs.[28,29] Moreover, the optical rotations, $[\alpha]_D^{20}$, for the three chiral ILs ([Ch][L-Ala], [Ch][Ser], and [Ch][Pro]) were measured in aqueous solution (Table 10). It was found that the optical rotations of these chiral ILs were quite different from those of the free amino acids. A similar phenomenon was reported previously by Allen et al.[9]

Table 10. Thermal Properties and Optical Rotations for [Ch][AA] ILs

entry	ILs	T_g/°C	T_d/°C	$[\alpha]_D^{20}$
1	[Ch][Gly]	−59	175	
2	[Ch][β-Ala]	−59	189	
3	[Ch][L-Ala]	−56	186	+1.50
4	[Ch][Pro]	−52	195	−44.63
5	[Ch][Ser]	−49	190	−2.63

Thermal Analysis. On the basis of DSC curves in Figure 6, no melting points were observed in the temperature range scanned for these five [Ch][AA] ILs. All of the [Ch][AA] ILs were liquids at room temperature. It was also seen from Table 10 that the T_g values ranged from (−45 to −60) °C, and the T_g varied with the structures of the anions. Generally, an increase in the size of amino acid anion resulted in a relatively high glass transition temperature. Moreover, the thermal gravimetric analysis (TGA) curves of these five [Ch][AA] ILs and [Ch]Cl were shown in Figure 7, and the derivative thermogravimetry (DTG) curves were also given in the Supporting Information (Figures S7−S12). As seen from the TGA and DTG curves, [Ch][Gly], and [Ch][L-Ala] were found to be decomposed in one step, and the decomposition processes of [Ch][β-Ala], [Ch][Ser], and [Ch][Pro] had more than one step. The T_d values increased as [Ch][Gly] < [Ch][L-Ala] < [Ch][β-Ala] < [Ch][Ser] < [Ch][Pro], and these values were

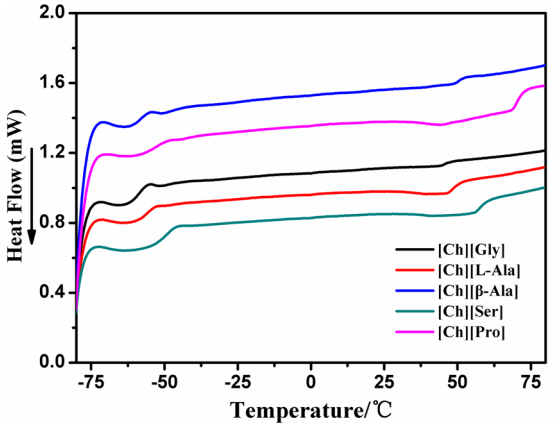

Figure 6. DSC curves for five [Ch][AA] ILs.

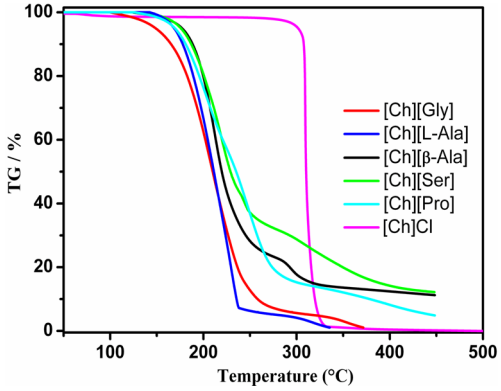

Figure 7. TGA curves for five [Ch][AA] ILs and [Ch]Cl.

in the range of (160 to 200) °C, which were comparable to those of other AAILs reported previously.[30] Of the AAILs tested, [Ch][Gly] gave the lowest T_d because of its smallest anion size. The introduction of a hydroxyl group and a pyrrolidinyl ring resulted in higher T_d values for [Ch][Ser] and [Ch][Pro]. Thus, it was demonstrated that the thermal stability of [Ch][AA] ILs were primarily related to the anion structures. A larger size of the anion tended to induce thermal decomposition of [Ch][AA] ILs at a higher temperature. In addition, it was also indicated that [Ch]Cl exhibited the best thermal stability among all of the salts investigated. The T_d value of [Ch]Cl was more than 300 °C, due to the strong ionic linkage between the cation $[Ch]^+$ and the anion Cl^-.

CONCLUSION

A series of [Ch][AA] ILs incorporating different amino acid anions were synthesized successfully by using natural product as feedstock, and their properties, namely, density, viscosity, refractive index, conductivity, and thermal stability, were investigated in detail at atmospheric pressure. From the experimental data, different densities, viscosities, and refractive indices were observed with a fixed cation ($[Ch]^+$) for different amino acids, because of different internal interactions (hydrogen bonding, van der Waals interactions, etc.) in each IL molecule. The density, viscosity, and refractive index were found to decrease linearly with the increase of temperature, while the conductivity increased exponentially with increasing temperature. The [Ch][AA] ILs also exhibited good thermal stability from the TGA curves. Furthermore, empirical equations (eqs 1, 2, 3, and 4) were used to correlate the experimental data of the measured physical properties, and thermal expansion coefficients were then calculated from the density data. The results indicated that the calculated values were in a good agreement with the measured results. The coefficient of thermal expansion was considered to be independent of temperature in the range of (298.15 to 353.15) K, as no appreciable change was observed with an increase of temperature. It is therefore believed that these present results will be added to the growing database on AAIL properties and can be applied for the design of many chemical processes such as catalysis, separation, and cellulose dissolution.

ASSOCIATED CONTENT

Supporting Information

Additional information as noted in text. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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