JOURNAL OF CHEMICAL & ENGINEERING DATA

ARTICLE

pubs.acs.org/jced

Synthesis and Thermophysical Properties of Low Viscosity Amino Acid-Based Ionic Liquids

Nawshad Muhammad,*[,†] Zakaria B. Man,[†] Mohamad Azmi Bustam,[†] M. I. Abdul Mutalib,[†] Cecilia D. Wilfred,[‡] and Sikander Rafiq[†]

[†]PETRONAS Ionic Liquid Center Chemical Engineering Department and [‡]Fundamental and Applied Sciences Department, Universiti Teknologi PETRONAS, Tronoh-31750, Perak, Malaysia

ABSTRACT: Nowadays ionic liquids are in the focus of scientific interest owing to their attractive properties. In this context, a series of amino acid-based ionic liquids (AAILs; EmimGly, EmimAla, EmimPro, and EmimSer) were synthesized and characterized by NMR and elemental analysis. Thermophysical properties such as density and viscosity were measured in the temperature range of T = (293.15 to 353.15) K and refractive index in the temperature range of T = (293.15 to 333.15) K. The thermal expansion coefficient values were calculated from the acquired experimental density values for T = (293.15 to 363.15) K. A thermogravimetric analyzer (TGA) was used to investigate the thermal degradation behavior of synthesized ionic liquids.

INTRODUCTION

Ionic liquids which are organic salts with melting points less than 100 °C are in the focus of green chemists as alternative solvents owing to their attractive properties such as chemical and thermal stability, nonflammability, and immeasurably low vapor pressure and designable solvents.[1,2] The first observation of an ionic liquid occurred in 1914 ([$EtNH_3$][NO_3], mp 13 to 14 °C). It was the development of modern ionic liquids that really accelerated research in this area during the past decade.[3] Ionic liquids are mainly consisting of organic cations and inorganic or organic anions. So there is a great possibility to design and tune their properties for various applications just by careful selection of the cation or anion or both,[4] or by incorporating the various functional groups (sulfonic acid, fluorous chain, ether, alcohol, carboxylic, thiols, nitrile amine, and amide)[5−9] to the structure for imparting the desired properties.[10] In this aspect, Fukumoto et al.[11] synthesized a new class of amino acid-based ionic liquids (AAILs). While measuring Kamlet−Taft parameters for these ionic liquids they find out that these ionic liquids have a high hydrogen bond basicity that is useful for dissolution of biomaterials, such as DNA, cellulose, and other carbohydrates.[12] Because of the functionality of amino acids, their ionic liquids should provide a variety of applications, such as intermediates for peptide synthesis, chiral solvents, functional materials, and biodegradable ionic liquids in the field of industrial and pharmaceutical chemistry.[13] For the investigation of the synthesis and the application of ionic liquids in the field of catalysis, separation, cellulose dissolution, and electrochemistry, their thermophysical properties are very important for analysis.

In this work, four AAILs, 1-ethyl-3-methylimidazolium aminoethanic acid (EmimGly), 1-ethyl-3-methylimidazolium L-α-aminopropionic acid (EmimAla), 1-ethyl-3-methylimidazolium 2-amino-3-hydroxypropionic acid (EmimSer), and 1-ethyl-3-methylimidazolium (S)-2-pyrrolidinecarboxylic acid (EmimPro) were synthesized by different approaches, as reported by Fukumoto et al.[11] The general route for the synthesis of these ionic liquids is depicted in Figure 1. For these synthesized ionic liquids the thermophysical properties (such as density, viscosity, and refractive index) have been measured at atmospheric pressure and at several temperatures. The values of the thermal expansion coefficient were determined from the results of density values as a function of temperature. The thermal degradation behaviors of these ionic liquids were studied by thermogravimetric analysis.

EXPERIMENTAL SECTION

Materials. All of the starting materials used were of analytical grade. These include 1-ethyl-3-methylimidazolium hydrogen sulfate (Merck), ethanol (Sigma), glycine, L-alanine, L-serine, and L-proline (Merck), barium hydroxide (Sigma Aldrich), and Millipore grade water.

Synthesis of AAILs. The ionic liquids EmimGly, EmimAla, EmimSer, and EmimPro were synthesized by the procedure as follows.

In the first step EmimOH aqueous solution was synthesized from 1-ethyl-3-methylimidazolium hydrogen sulfate by adding $EmimHSO_4$ (0.05 mol) into an equimolar aqueous solution of $Ba(OH)_2$ (dissolve in boiling water) and stirring for 12 h. In the second step, it was filtered, and EmimOH containing filtrate was neutralized with an equimolar aqueous solution of amino acid by stirring at room temperature for 12 h. After neutralization, water was evaporated under soft vacuum at 50 °C. The excess amino acid was precipitate by adding ethanol. After filtration the ionic liquid was dried using a vacuum rotary and followed by vacuum oven.

Characterization. ^1H NMR spectra were taken in dimethyl sulfoxide (DMSO)-d_6 solvent and recorded on a Bruker Avance 300 spectrometer, and a CHNS-932 (LECO instruments) was used for elemental analysis

Before water measurement, 5 g of the each sample was taken and dried in a vacuum oven for 4 h at 80 °C. A coulometric Karl

Received: March 8, 2011
Accepted: May 18, 2011
Published: May 27, 2011

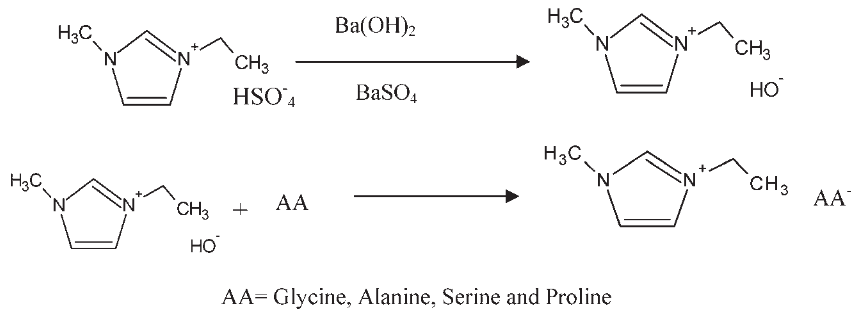

Figure 1. General route for the synthesis of the above ionic liquids.

Table 1. Mass Fraction of Water *w* for AAIL Synthesized Ionic Liquids

$10^6\ w$			
EmimGly	EmimAla	EmimSer	EmimPro
296	255	256	227

Table 2. Experimental Dynamic Viscosities η for AAILs as a Function of Temperature

	$\eta/(\mathrm{mPa\cdot s})$			
T/K	EmimGly	EmimAla	EmimSer	EmimPro
293.15	80.37	235.36	611.87	626.95
298.15	61.51	171.19	410.86	426.12
303.15	47.75	126.60	279.82	295.17
308.15	37.79	93.87	196.70	210.2
313.15	30.31	72.02	142.28	153.57
318.15	24.89	56.62	105.80	114.27
323.15	20.64	45.13	80.49	87.05
328.15	17.33	36.56	62.48	67.61
333.15	14.72	30.10	49.31	54.04
338.15	12.64	25.02	39.63	43.43
343.15	10.94	21.21	32.36	35.47
348.15	9.55	18.05	26.82	29.36
353.15	8.38	15.51	22.47	24.50

Fischer titrator, DL 39 (Mettler Toledo), was used to determine the water content of the above synthesized ILs, using the Hydranal coulomat AG reagent (Riedel-de Haen). The measurement for each IL was made in triplicate, and the average values are reported in Table 1.

Property Measurements. All of the synthesized ionic liquids before measuring their properties were purified under low pressure by keeping them in a vacuum oven for 4 h at 80 °C. Millipore grade water with known viscosity, density, and refractive index values was used for the calibration of instruments. The instruments were also calibrated with ionic liquids, namely, 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, $[C_6Mim]Tf_2N$ Tf_2N, bis(2-hydroxyethyl)ammonium acetate, BHEAA, and 1-propyronitrile-3-butylimidazolium bromide, $[C_2CN\ Bim]Br$, for which the data were already established by our research group.[14−16]

Density and Viscosity Measurements. Anton Paar viscometer (model SVM3000) was used for measurement of density and viscosity at temperature range of (293.15 to 353.15) K. The temperature was controlled to within ± 0.01 °C. The reproducibility of the measurements were 0.4 % and $\pm\ 4.70\cdot10^{-4}$ $\mathrm{g\cdot cm^{-3}}$ for viscosity and density, respectively.[14−16]

Refractive Index Measurements. The refractive indices of all samples were determined using an ATAGO programmable digital refractometer (RX-5000α) with a measuring accuracy of $\pm\ 4\cdot10^{-5}$ at the temperature range of (293.15 to 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.[14−16]

Thermal Decomposition. A Perkin-Elmer Pyris V-3.81 thermal gravimetric analyzer was used to measure the onset and thermal decomposition temperature for the above synthesized ionic liquids. The samples were placed in an aluminum pan under nitrogen atmosphere at a heating rate of 10 $\mathrm{°C\cdot min^{-1}}$ with temperature accuracy better than ± 3 °C.

■ RESULTS AND DISCUSSION

The synthesis of these ionic liquids using the above-mentioned method is quite easy as compared to reported by Fukumoto et al.[11] In Fukumoto et al. reported method, the EmimOH was prepared from EmimBr through an anion exchange resin column which was time-consuming due to the slow exchange of Br with OH of resin. Also a large batch of ionic liquids could not prepared by this method. While the method presented in this paper has the potential to synthesis the EmimOH in a short time, and also a large batch of ionic liquids can be prepared. Moreover, this method can also be used for the preparation of other dialkylimidazolium hydroxides from dialkylimidazolium-based ILs having a hydrogen sulfate anion. The estimated purities of the present synthesized ionic liquids, namely, EmimGly, EmimAla, EmimSer, and Emimpro, are 97.8 %, 97.5 %, 97.3 %, and 96.9 %, respectively. The results acquired by NMR and elemental analysis for above synthesized ionic liquids confirmed their structures.

EmimGly ^{1}H NMR (DMSO): 1.42 (t, 3H,), 2.76 (s, 2H), 3.83 (s, 3H), 4.25 (q, 2H,), 7.73 (s, 1H), 7.82 (s, 1H), 9.60 (s, 1H). Elemental analysis (%), calculated: C 51.87, H 6.8, N 22.68, O 17.27; found: C 51.43, H 8.49, N 22.55, and O 17.35.

EmimAla ^{1}H-NMR (DMSO): 1.04 (d, 3H), 1.43 (t, 3H), 2.91 (q, 1H), 3.83 (s, 3H), 4.22 (q, 2H), 7.75 (s, ^{1}H), 7.84 (s, 1H), 9.72 (s, 1H).

Elemental analysis (%), calculated: C 54.25, H 8.59, N 21.08, O 16.05; found: C 54.01, H 8.68, N 21.06, and O 16.10.

EmimSer ^{1}H NMR (DMSO): 1.41 (t, 3H), 2.88 (t, 1H), 3.25 (m, 2H), 3.83 (s, 3H), 4.21 (q, 2H), 7.78 (s, 1H), 7.80 (s, 1H), 9.47 (s, 1H).

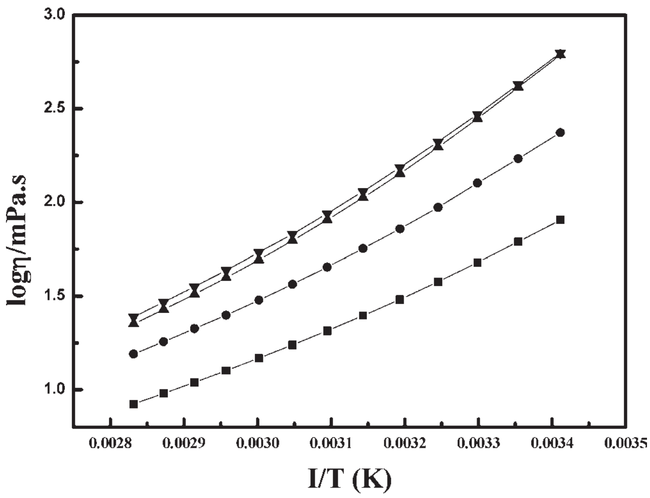

Figure 2. Viscosities as a function of temperature for: ■, EmimGly; ●, EmimAla; ▲, EmimSer and ▼, EmimPro.

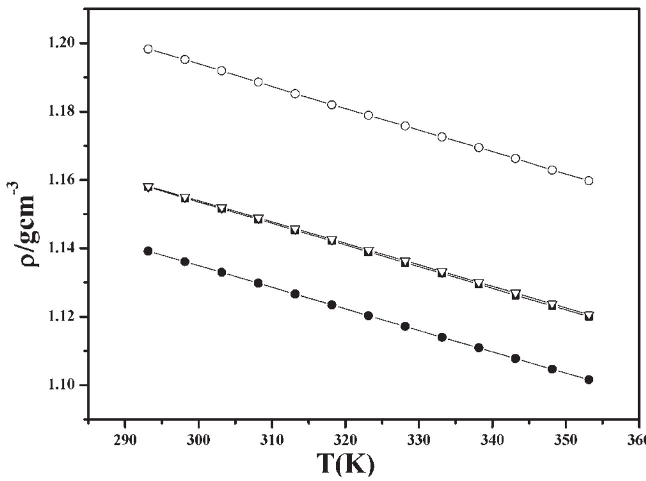

Figure 3. Densities as a function of temperature for ●, EmimAla; □, EmimGly; △, EmimPro and ○, EmimSer.

Table 3. Experimental Densities ρ for AAILs as a Function of Temperature

T/K	ρ/(g·cm^{-3})			
	EmimGly	EmimAla	EmimSer	EmimPro
293.15	1.1580	1.1392	1.1983	1.1581
298.15	1.1547	1.1361	1.1952	1.1550
303.15	1.1516	1.1330	1.1919	1.1519
308.15	1.1485	1.1298	1.1886	1.1489
313.15	1.1453	1.1266	1.1852	1.1457
318.15	1.1422	1.1235	1.182	1.1426
323.15	1.1390	1.1203	1.1789	1.1395
328.15	1.1358	1.1172	1.1758	1.1363
333.15	1.1327	1.1140	1.1726	1.1332
338.15	1.1295	1.1109	1.1695	1.1300
343.15	1.1263	1.1078	1.1663	1.1269
348.15	1.1232	1.1047	1.1629	1.1237
353.15	1.1201	1.1016	1.1598	1.1206

Table 4. Experimental Refractive Indices n_D for AAILs as a Function of Temperature

T/K	n_D			
	EmimGly	EmimAla	EmimPro	EmimSer
293.15	1.50628	1.50586	1.51205	1.51523
298.15	1.50473	1.50410	1.51069	1.51372
303.15	1.50313	1.50246	1.50932	1.51229
308.15	1.50154	1.50072	1.50791	1.51073
313.15	1.49988	1.49908	1.50654	1.50924
318.15	1.49827	1.49735	1.50511	1.50774
323.15	1.49657	1.49568	1.50372	1.50621
328.15	1.49488	1.49395	1.50224	1.50454
333.15	1.49321	1.49228	1.50083	1.50310

Elemental analysis (%), calculated: C 50.22, H 7.96, N 19.52, O 22.29; found: C 50.01, H 8.20, N 19.32, and O 22.48.

Emimpro ^{1}H NMR (DMSO): 1.43 (t, 3H), 1.46 (m, 1H), 1.54 (m, 1H), 1.68 (1H), 1.79 (m, 1H), 2.62 (1H), 2.94 (m, 1H) 3.16 (1H), 3.87 (s, 3H), 4.24 (q, 2H), 7.74 (s, 1H), 7.82 (s, 1H), 9.63 (s, 1H).

Elemental analysis (%), calculated: C 49.69, H 8.92, N 15.81, O 25.58; found: C 49.16, H 9.85, N 15.02, O 25.98.

Viscosity. Table 2 shows the effect of temperature on viscosities of AAILs in the temperature range of (293.15 to 353.15) K. The structures of AA anions have a pronounced effect on the viscosities of the AAILs. The viscosities of the AAILs increased with the increase of AA anion chain length due to the increase in the internal resistance, for mobility of the AAILs. Also, the functional group of AA anions increased the viscosity of AAILs due to its tendency to form hydrogen bonds.[17] It has been observed that the viscosities of the present AAILs increase as EmimGly < EmimAla < EmimSer < EmimPro. As concerns the structure moiety of each ionic liquid, the interactions (hydrogen bonding, van der Waals interactions and size of amino acid anion) were found to increase as EmimGly < EmimAla < EmimSer < EmimPro. This trend in viscosities of the present ionic liquids is in good agreement with that reported by Zhang et al.[17] for other AAILs containing a [$aP_{4,4,4,3}$] cation with similar anions (viscosities for [$aP_{4,4,4,3}$][Gly], [$aP_{4,4,4,3}$][Ala], [$aP_{4,4,4,3}$][Ser], and [$aP_{4,4,4,3}$][Pro] were 713.9 mPa·s, 758.0 mPa·s, 1341.7 mPa·s, and 1772.8 mPa·s, respectively, at 298.15 K). The temperature has an inverse effect on viscosity as shown in Figure 2.

Density. Table 3 shows the densities of AAILs in the temperature range from (293.15 to 353.15) K. The value measured in this work was in the range as reported elsewhere (1.1589, 1.1209 for EmimGly and EmimAla, respectively) at 298.15 K.[13,19] It has been observed that the densities increased as EmimAla < EmimGly < EmimPro < EmimSer. The present AAILs showed a similar trend in densities as reported for other AAILs having the same AA anions with different cations, that is, [$aP_{4,4,4,3}$] and [$P_{8,8,8,8}$].[17,18] The densities reported by Zhang et al.[17] for [$aP_{4,4,4,3}$][Ala], [$aP_{4,4,4,3}$][Gly], [$aP_{4,4,4,3}$][Pro], and [$aP_{4,4,4,3}$]-[Ser] were 0.9858 g·cm^{-3}, 0.9973 g·cm^{-3}, 1.0047 g·cm^{-3}, and 1.0262 g·cm^{-3}, respectively, at 298.15 K. The temperature was observed to have an inverse effect on density as shown in Figure 3.

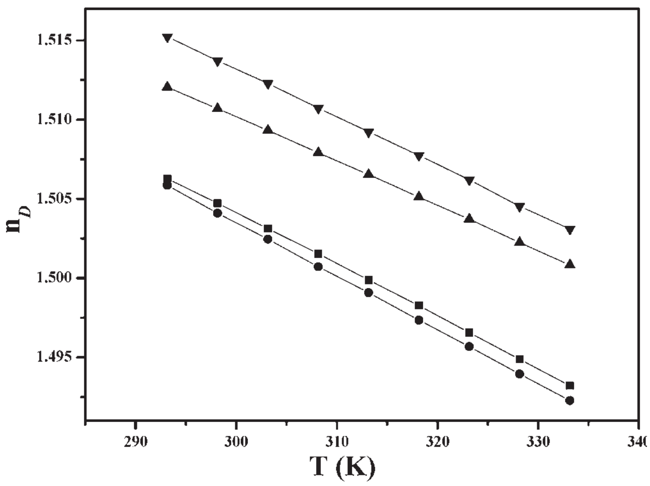

Figure 4. Refractive index as a function of temperature: ●, EmimAla; ■, EmimGly; ▲, EmimPro; and ▼, EmimSer.

Table 5. Fitting Parameter Values of eq 1 and the Standard Deviations (SDs) Using eq 4

ionic liquid	A_0	A_1	SD	R^2
EmimGly	−3.87052	1682.46066	0.02091	0.9980
EmimAla	−4.60318	2031.47792	0.02789	0.9975
EmimSer	−5.68207	2464.24945	0.03724	0.9970
EmimPro	−5.50911	2418.68245	0.03332	0.9975

Refractive Index. Table 4 presents the refractive index of the above synthesized ionic liquids. It has been noted that refractive index values were in the same range as reported for other ionic liquids.[15] It has been observed that the refractive index increased as EmimGly < EmimAla < EmimPro < EmimSer. The high refractive index values of EmimSer could be due to the extra electron mobility around the additional OH group in serinate anion. The refractive index was observed to be linearly decreasing with an increase in temperature as shown in Figure 4.

The viscosity η, the density ρ, and the refractive indices n_D of experimental values were fitted by the least-squares method using the following reported equations:[14−16]

$$\log \eta/(\mathrm{mPa \cdot s}) = A_0 + (A_1/T) \quad (1)$$

$$\rho/(\mathrm{g \cdot cm^{-1}}) = A_2 + A_3 T \quad (2)$$

$$n_D = A_4 + A_5 T \quad (3)$$

where η, ρ, and n_D denote the viscosity, the density, and the refractive indices of the present synthesized ionic liquids, res pectively. A_0, A_1, A_2, A_3, A_4, and A_5 are correlation coefficients. T is the Kelvin temperature. The correlation coefficients were estimated by least-squares fitting method using eqs 1, 2, and 3. The values of least-squares fitting method are presented together with standard deviation (SD) values in Tables 5, 6, and 7. The standard deviation values were calculated by using the following eq 4:[14−16]

Table 6. Density Fitting Parameter Values of eq 2 and the Standard Deviations (SDs) Using eq 4

ionic liquid	A_2	A_3	SD	R^2
EmimGly	1.34307	$-6.31538 \cdot 10^{-4}$	$4.6183 \cdot 10^{-5}$	0.9999
EmimAla	1.32334	$-6.28132 \cdot 10^{-4}$	$5.21276 \cdot 10^{-5}$	0.9999
EmimSer	1.38658	$-6.42308 \cdot 10^{-4}$	$1.47354 \cdot 10^{-4}$	0.9999
EmimPro	1.34174	$-6.25941 \cdot 10^{-4}$	$4.94597 \cdot 10^{-5}$	0.9999

Table 7. Fitting Parameter Values of eq 3 and the Standard Deviations (SDs) Using eq 4

ionic liquid	A_4	A_5	SD	R^2
EmimGly	1.60236	$-3.2742 \cdot 10^{-4}$	$6.64963 \cdot 10^{-5}$	0.9999
EmimAla	1.60521	$-3.3900 \cdot 10^{-4}$	$2.59119 \cdot 10^{-5}$	0.9999
EmimSer	1.59441	$-2.8057 \cdot 10^{-4}$	$4.11186 \cdot 10^{-5}$	0.9999
EmimPro	1.60441	$-3.0405 \cdot 10^{-4}$	$5.98853 \cdot 10^{-5}$	0.9998

$$\mathrm{SD} = \sqrt{\frac{\sum_i^{n_{dat}} (Z_{exp} - Z_{cal})^2}{n_{dat}}} \quad (4)$$

where SD, n_{dat}, Z_{exp}, and Z_{cal} are the standard deviation, number of experimental points, and experimental and calculated data values, respectively.

The values of densities calculated for above synthesized ionic liquids were used to calculate for another thermophysical property named as the thermal expansion coefficient (α) (Table 8) by using the following eq 5:[14−16]

$$\alpha_P = -\frac{1}{\rho}\left(\frac{\delta\rho}{\delta T}\right)_P = -\frac{A_3}{A_2 + A_3 T} \quad (5)$$

where α_P, ρ, and T are the thermal expansion coefficient, density, and absolute temperature, respectively, whereas A_2 and A_3 are the fitting parameters of eq 2. The thermal expansion coefficient (α_P) was also known as volume expansivity. It can be observed from Table 8 that the coefficients of thermal expansion of above synthesized ionic liquids do not change appreciably with respect to temperature and show their independence of temperature. The values obtained for above synthesized ionic liquids were also found similar to those reported for imidazolium, pyridinium, phosphonium, and ammonium-based ILs, ($5.0 \cdot 10^{-4}$ to $6.5 \cdot 10^{-4}$) K^{-1}.[20,21]

Thermal decomposition values of the above synthesized ionic liquids are reported in terms of onset temperature and thermal decomposition temperature T_d as shown in Table 9. It is clear that the thermal decomposition increases as EmimGly < EmimAla < EmimSer < EmimPro. The thermal decomposition temperature values measured in this work were found to be higher than the reported values of some AAILs ionic liquids (EmimAla and BmimGly are 212 °C (485 K) and 483.5 K, respectively).[12,22] For EmimGly, the T_d measured (499 K) was high compared to BmimGly (483.5 K) because the increase in alkyl chain length on cation decreases the thermal decomposition of IL.[23] However in case of EmimAla, the difference in T_d might be due to a different method applied in the synthesis of these ionic liquids or due to difference in the experimental setup, that is, heating rates and type of pan used during thermal analysis.

Table 8. Thermal Expansion Coefficient Values of Presented Ionic Liquids as a Function of Temperature Using eq 5

T/K	$\alpha \cdot 10^4/(K^{-1})$			
	EmimGly	EmimAla	EmimSer	EmimPro
293.15	5.42	5.51	5.36	5.40
298.15	5.44	5.52	5.37	5.41
303.15	5.45	5.54	5.38	5.43
308.15	5.47	5.56	5.40	5.44
313.15	5.48	5.57	5.41	5.46
318.15	5.50	5.59	5.43	5.47
323.15	5.51	5.60	5.44	5.49
328.15	5.53	5.62	5.46	5.50
333.15	5.55	5.63	5.47	5.52
338.15	5.56	5.65	5.49	5.53
343.15	5.58	5.67	5.50	5.55
348.15	5.59	5.68	5.52	5.57
353.15	5.61	5.70	5.53	5.58

Table 9. Onset T_s and Decomposition T_d Temperatures for AAILs

property	EmimGly	EmimAla	EmimSer	EmimPro
T_s/K	475	482	489	528
T_d/K	499	504	512	558

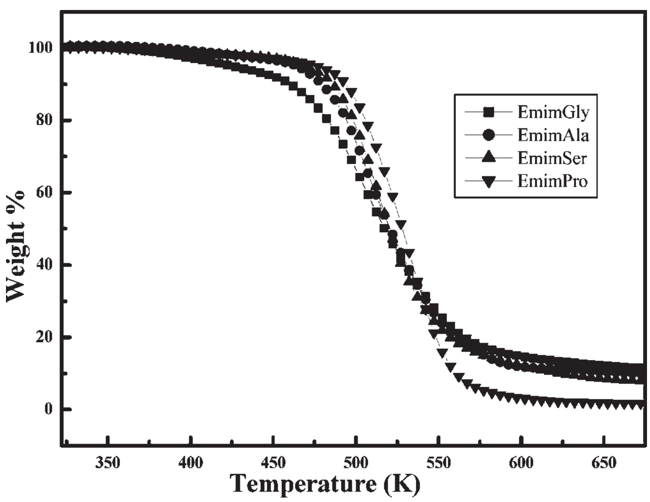

Figure 5. Thermograph analysis of ■, EmimGly; ●, EmimAla; ▲, EmimSer; and ▼, EmimPro as a function of temperature.

Thermographs of the present AAILs have been shown in Figure 5.

■ CONCLUSION

AAILs of low viscosities were synthesized by another approach as reported by Fukumoto et al.[11] The method used here has the potential to synthesize the ionic liquids in a short time with a large quantity. The experimental values of density and dynamic viscosity at a temperature range from (293.15 to 353.15) K and refractive index from (298.15 to 333.15) K were measured and reported for AAILs. Different viscosities, densities, and refractive indices were observed with a fixed cation ($Emim^+$) for different amino acids, because of different internal interactions (hydrogen bonding, van der Waals interactions, etc.) in each ionic liquid molecule. The coefficient of thermal expansion was considered to be independent of temperature in the range of (293.15 to 353.15) K, as no appreciable change was observed with the increase in temperature. The thermal decomposition temperatures of these ionic liquids were measured and found in the order EmimGly < EmimAla < EmimSer < EmimPro.

■ AUTHOR INFORMATION

Corresponding Author

*Tel.: +6053687702. Fax: +6053687598. E-mail address: nawshadchemist@yahoo.com.

Funding Sources

This work was supported by PETRONAS Ionic Liquid Center, Department of Chemical Engineering, Universiti Teknologi PETRONAS, Malaysia.

■ REFERENCES

(1) Li, R. X. *Green solvents: synthesis and application of ionic liquids*; China Chemical Industry Press: Beijing, 2005; pp 298−300.

(2) Earle, M. J.; Seddon, K. R. Ionic liquids. Green solvents for the future. *Pure Appl. Chem.* **2000**, *72*, 1391–1398.

(3) Plechkova, N. V.; Seddon, K. R. Applications of ionic liquids in the chemical industry. *Chem. Soc. Rev.* **2008**, *37*, 123.

(4) Torrecilla, J. S.; Palomar, J.; Garcí, J. N.; Rodríguez, F. Effect of Cationic and Anionic Chain Lengths on Volumetric, Transport, and Surface Properties of 1-Alkyl-3-methylimidazolium Alkylsulfate Ionic Liquids at (298.15 and 313.15) K. *J. Chem. Eng. Data* **2009**, *54*, 1297–1301.

(5) Zhang, Q.; Li, Z.; Zhang, J.; Zhang, S.; Zhu, L.; Yang, J.; Zhang, X.; Deng, Y. Physicochemical Properties of Nitrile-Functionalized Ionic Liquids. *J. Phys. Chem. B* **2007**, *111*, 2864–2872.

(6) Zhang, S.; Chen, Y.; Li, F.; Lu, X.; Dai, W.; Mori, R. Fixation and conversion of CO_2 using ionic liquids. *Catal. Today* **2006**, *115*, 61–69.

(7) Liu, X.-M.; Song, Z.-X.; Wang, H.-J. Density Functional Theory Study on the-SO_3H Functionalized Acidic Ionic Liquids. *Struct. Chem.* **2009**, *20*, 509–51.

(8) Fei, Z.; Ang, W. H.; Zhao, D.; Scopelliti, R.; Zvereva, E. E.; Katsyuba, S. A.; Dyson, P. J. Revisiting Ether-Derivatized Imidazolium-Based Ionic Liquids. *J. Phys. Chem. B* **2007**, *111*, 10095–10108.

(9) Nockemann, P.; Thijs, B.; Parac-Vogt, T. N.; Hecke, K. V.; Meervel, L. V.; Tinant, B.; Hartenbach, I.; Schleid, T.; Ngan, V. T.; Nguyen, M. T.; Binnemans, K. Carboxyl-Functionalized Task-Specific Ionic Liquids for Solubilizing Metal Oxides. *Inorg. Chem.* **2008**, *47*, 9987–9999.

(10) Davis, J. H. Task-Specific Ionic Liquids. *Chem. Lett.* **2004**, *33*, 1072–1077.

(11) Fukumoto, K.; Yoshizawa, M.; Ohno, H. Room Temperature Ionic Liquids from 20 Natural Amino Acids. *J. Am. Chem. Soc.* **2005**, *127*, 2398–2399.

(12) Ohno, H.; Fukumoto, K. Amino Acid Ionic Liquids. *Acc. Chem. Res.* **2007**, *40*, 1122–1129.

(13) Yang, J. Z.; Zhang, Q. G.; Wang, B.; Tong, J. Study on the Properties of Amino Acid Ionic Liquid EMIGly. *J. Phys. Chem. B* **2006**, *110*, 22521–22524.

(14) Muhammad, A.; Mutalib, M. I. A.; Wilfred, C. D.; Murugesan, T.; Shafeeq, A. Thermophysical properties of 1-hexyl-3-methyl imidazolium based ionic liquids with tetrafluoroborate, hexafluorophosphate and bis(trifluoromethylsulfonyl)imide anions. *J. Chem. Thermodyn.* **2008**, *40*, 1433–1438.

(15) Ziyada, A. K.; Wilfred, C. D.; Bustam, M. A.; Man, Z.; Murugesan, T. Thermophysical Properties of 1-Propyronitrile-3-alkylimidazolium Bromide Ionic Liquids at Temperatures from (293.15 to 353.15) K. *J. Chem. Eng. Data* **2010**, *55*, 3886–3890.

(16) Kurnia, K. A.; Wilfred, C. D.; Murugesan, T. Thermophysical properties of hydroxyl ammonium ionic liquids. *J. Chem. Thermodyn.* **2009**, *41*, 517–521.

(17) Zhang, Y. Q.; Zhang, S. J.; Lu, X. M.; Zhou, Q.; Fan, W.; Zhang, X. P. Dual Amino-Functionalized Phosphonium Ionic Liquids for CO_2 Capture. *Chem.—Eur. J.* **2009**, *15*, 3003.

(18) Kagimoto, J.; Taguchi, S.; Fukumoto, K.; Ohno, H. Hydrophobic and low-density amino acid ionic liquids. *J. Mol. Liq.* **2010**, *153*, 133–138.

(19) Fang, D. W.; Guan, W.; Tong, J.; Wang, Z. W.; Yang, J. Z. Study on Physicochemical Properties of Ionic Liquids Based on Alanine [$C_n$mim][Ala] (n = 2, 3, 4, 5, 6). *J. Phys. Chem.* **2008**, *112*, 7499–7505.

(20) Huddleston, J. G.; Visser, A. E.; Reichert, W. M.; Willauer, H. D.; Broker, G. A.; Rogers, R. D. Characterization and comparison of hydrophilic and hydrophobic room temperature ionic liquids incorporating the imidazolium cation. *Green Chem.* **2001**, *3*, 156–164.

(21) Taib, M. M.; Ziyada, A. K.; Wilfred, C. D.; Murugesan, T. Thermophysical properties of 1-propyronitrile-3-hexylimidazolium bromide + methanol at temperatures (293.15 to 323.15) K. *J. Mol. Liq.* **2010**, *158* (2), 101–104.

(22) Guan, W.; Xue, W. F.; Li, N.; Tong, J. Enthalpy of Solution of Amino Acid Ionic Liquid 1-Butyl-3-methylimidazolium Glycine *J. Chem. Eng. Data* **2008**, *53*, 1401–1403.

(23) Yunus, N. M.; Mutalib, M. I. A.; Man, Z.; Bustam, M. A.; Murugesan, T. Thermophysical properties of 1-alkylpyridinum bis-(trifluoromethylsulfonyl)imide ionic liquids. *J. Chem. Thermodyn.* **2010**, *42*, 491–495.