Thermophysical properties of 1-hexyl-3-methyl imidazolium based ionic liquids with tetrafluoroborate, hexafluorophosphate and bis(trifluoromethylsulfonyl)imide anions

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ARTICLE INFO

ABSTRACT

The thermophysical properties of 1-hexyl-3-methyl imidazolium based hydrophobic room temperature ionic liquids (RTILs); with tetrafluoroborate (BF_4), hexafluorophosphate (PF_6), and bis(trifluoromethylsulfonyl)imide (Tf_2N) anions, namely density ρ (298.15 to 348.15) K, dynamic viscosity η (288.2 to 348.2) K, surface tension σ (298.15 to 338) K, and refractive index n_D (302.95 to 332.95) K have been measured. The coefficients of thermal expansion α_p values were calculated from the experimental density data using an empirical correlation. The thermal stability of all ILs is also investigated at two different heating rates (10 and 20) $°C \cdot min^{-1}$) using thermogravimetric analyzer (TGA). The experimental results presented in this study reveal that the choice of anion type shows the most significant effect on the properties of ILs. The chloride and water contents of ILs (as impurities) are also investigated and reported in the present work.

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1. Introduction

Ionic liquids (ILs) are defined as molten salts that are liquid over a wide temperature range and are comprised of cations (organic) and anions (organic/inorganic). ILs are also known as "designer solvents" as they can be designed by appropriate combination of various anions and cations. In the recent times, the most commonly studied ILs normally contain, imidazolium, ammonium, phosphonium, pyridinium, pyrrolidinium cations, and $[BF_4]^-$, $[PF_6]^-$, $(CF_3SO_2)_2N^- = [Tf_2N]^-$, $(CF_3SO_3)^- = [OTf]^-$, and $CF_3CO_2^-$, anions [1,2]. ILs have gained attention as a potential solvent in a variety of separation processes, over conventional organic solvents, due to their unique properties such as negligible vapour pressure, good thermal stability, wide liquid range, and tunability. The determination and understanding of basic physical and transport properties of ILs, such as density (for equipment sizing), viscosity (for fluid flow and diffusion of gases), surface tension, refractive index, thermal decomposition (to set the feasible temperature operating range), and thermal expansion, is vital for the process design and development of contacting equipments [3]. In spite of the importance and utility of ILs, accurate values for many of their fundamental physical, chemical, and thermodynamic properties are either scarce or even mostly absent [4]. In the recent past, the investigation on the properties of ILs has increased considerably. However, due to the large discrepancies for characterization data

of ILs in the published literature, there is an immense need of generating reliable and accurate data along with the purity and stability of the investigated IL samples [5]. The properties of ILs and their capacity to dissolve gases are significantly affected by the type of anion as compared to cation [6].

In this work, thermophysical properties of three ILs: 1-hexyl-3-methyl imidazolium tetraflouroborate; $[C_6mim][BF_4]$, 1-hexyl-3-methyl imidazolium hexaflourophosphate; $[C_6mim][PF_6]$ and 1-hexyl-3-methyl imidazolium bis(trifluoromethylsulfonyl)imide; $[C_6mim][Tf_2N]$ have been determined at atmospheric pressure and at temperatures (288.15 to 358.15) K. All the measurements were carried out at $T \leqslant 358$ K to avoid any chances of $[PF_6]^-$ hydrolysis/decomposition, producing HF, specifically when treated at very high temperatures or comes in contact with water [7–9]. The validation of data for physical properties of ILs reported here, is fortified by performing purity measurements of ILs in terms of chloride and water contents. The chloride and water impurities considerably alter the physical properties of ILs [10]. The coefficients of thermal expansion values of ILs are calculated from the density data as a function of temperature. A comparison between the experimental results of this work and the available literature data is also made.

2. Chemicals

Ionic liquids, such as $[C_6mim][BF_4]$ (CAS number 244193-50-8) and $[C_6mim][Tf_2N]$ (CAS number 382150-50-7), containing both water and chloride contents $\leqslant 100$ ppm whereas $[C_6mim][PF_6]$

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(CAS number 304680-35-1) with water ⩽100 ppm and chloride contents ⩽10 ppm, were purchased from Merck. All the ionic liquids obtained were of high purity grade with quoted purity of ⩾99.0%. Prior to their use, the ionic liquids were dried in a vacuum drier at 313 K and 76 cm of Hg for 3 days.

3. Experimental

All the IL samples were prepared in glass vials and closed with screw caps fitted with silicone septum, to ensure a secure seal and preventing their contact with moisture in air. The samples were taken from the vials with a syringe and immediately placed into the apparatus for each experimental measurement to avoid the humid effects of atmosphere.

3.1. Chloride and water contents

The chloride contents of all ILs were determined using a DL-55 autotitrator (Mettler Toledo) with 0.005 M $AgNO_3$ as the titrant. The water contents of ILs were investigated using a coulometric Karl Fischer titrator, DL 39 (Mettler Toledo), using Hydranal coulomat AG reagent (Riedel-de Haen). Each measurement was made in triplicate and the values are reported as an average with an accuracy of 5%.

3.2. Density

The density of ILs was measured with an Anton Paar, Oscillating U-tube density meter, (DMA 5000) at temperatures (298.15 to 358.15) K with an uncertainty of ±0.01 °C. The apparatus was calibrated by measuring the density of Millipore quality water at regular intervals according to the supplier instructions. The calibrated apparatus was also verified using few pure organic liquids of known densities. The overall precision in experimental density measurements for all samples was found to be better than $\pm 2 \cdot 10^{-5} \, \text{g} \cdot \text{cm}^{-3}$.

3.3. Dynamic viscosity

The viscosity of each RTIL was measured using cone and plate (CAP 2000, L-series), Brookfield viscometer at (288.2 to 348.2) K with a temperature control accuracy of ±0.2 °C. The viscometer was calibrated frequently according to the instructions using standard calibration fluids provided by the supplier. The viscometer was placed in a dry place and the viscosity measurement proceeded as soon as the sample was placed on viscometer plate. The sample is considered to be, no more in contact with the external environment, as soon as the cone is tightly pressed on plate. The viscometer was operated at rotational speed of 900 rpm using cone numbers 1 to 4, recommended for viscosity range (21 to 1667) MPa · s. The viscosity measurements were performed in triplicate and the results are reported as an average agreeing to within 10 MPa s.

3.4. Surface tension

The surface tension of each IL was measured with a spinning drop video tensiometer (SVT 20) using the standard method of measurements (dataphysics, instruments GmbH). All the readings were taken at temperatures (298.15 to 338.15) K with an accuracy of ±0.03 °C.

3.5. Refractive indices

The refractive indices of all RTILs were determined using ATAGO programmable digital refractometer (RX-5000 alpha) with

a measuring accuracy of $\pm 4 \cdot 10^{-5}$. All the measurements were performed at (302.95 to 332.95) K with a temperature control accuracy of ±0.05 °C. The apparatus was calibrated by measuring the refractive index of Millipore quality water before each series of measurements according to the instructions and checked for pure liquids with known refractive indices.

3.6. Thermal decomposition

Thermal stability of ILs was investigated using a thermogravimetric analyzer (TGA, Perkin–Elmer, Pyris V-3.81) at temperatures (40 to 700) °C. The effect of temperature on the decomposition of ILs, using platinum pan under N_2 atmosphere, was studied at two different heating rates, *i.e.*, (10 and 20) °C · min^{-1} with temperature accuracy better than ±3 °C.

4. Results and discussion

The chloride and water contents of dried ILs are found to be in order [PF₆] > [BF₄] > [Tf₂N], respectively as shown in table 1. The varying degree of water contents associated with ILs when compared with the literature data could be due to the difficulty involved in drying at very low moisture contents as well as the drying method involved.

The physical properties of ILs investigated in the present work is compared with the recent literature value at 298.15 K and 302.95 K and listed in table 2. The present experimental values of density, dynamic viscosity, surface tension, and calculated values of coefficients of thermal expansion for ILs are presented in table 3. All the physical properties of ILs investigated in this work showed high dependence on the molar mass of anion and decreased with an increase in temperature. The experimental density values of ILs were higher than water, ranging from 1.14532 to 1.37213 g · cm^{-3} and found to be in order [C₆mim][Tf₂N] > [C₆mim][PF₆] > [C₆mim][BF₄].

A comparison of density, dynamic viscosity, and surface tension values of ILs at several temperatures, studied in this work and the available literature data, is made and illustrated in figures 1 to 3.

The high discrepancies in the dynamic viscosity values of ILs when compared with the literature may be due to the difference in chloride and water contents, the same effect is also observed and reported by Wang et al. [12]. For a common cation, a linear variation of surface tension with temperature is observed for all ILs. The surface tension values decreased with the reduction in anion size in case of [BF₄]⁻ and [PF₆]⁻ anions, which are in good agreement with the reported literature [13]. However, the reason for lower surface tension values in case of [Tf₂N]⁻ anion is not clear. The surface tension values are higher in this work than the reported values of Pereiro et al. [4] for [C₆mim][PF₆], as shown in figure 3.

The refractive indices of ILs at temperatures (302.95 to 332.95) K are measured and presented in table 4, due to their importance of relation with polarizability/dipolarity of the medium. The values of refractive indices decreased with increase in temperature and the values are found to be in same order as that of density, *i.e.*, [C₆mim][Tf₂N] > [C₆mim][PF₆] > [C₆mim][BF₄]. The variation of refractive index of ILs with temperature is shown in figure 4 along with the available literature.

TABLE 1
Chloride contents and water contents of dried ILs

Impurities (ppm)	[C₆mim][BF₄]	[C₆mim][PF₆]	[C₆mim][Tf₂N]
Chloride contents	34	45	28
Water contents	324	456	268
		300 [11]	
		472 [14]	

TABLE 2
Experimental values of densities (ρ), dynamic viscosities (η), surface tension (σ) at $T = 298.15$ K and refractive indices (n_D) at $T = 302.95$ K, present work and literature

	[C$_6$mim][BF$_4$]		[C$_6$mim][PF$_6$]		[C$_6$mim][Tf$_2$N]	
	This work	Lit.	This work	Lit.	This work	Lit.
ρ/(g · cm^{-3})	1.14532	1.1493 [15] 1.1481 [16]	1.29341	1.29366 [4] 1.2937 [11] 1.29 [14] 1.2935 [16]	1.37213	1.37081 [19]
η/(MPa · s)	102	314 [10] 279.86[a] [20]	607	475.66 [4] 560 [17] 585 [14]	68	60[c] [21] 70.29 [23]
σ/(mN · m^{-1})	36.8	n.a.	42.1	37.1 [4] 43.4 [14]	32.5	35[c] [21] 35.79[d] [22]
n_D	1.42640	n.a.	1.41694	1.41643[b] [11]	1.42958	n.a.

[a] At 298.2 K.
[b] At 303.15 K.
[c] At 298 K.
[d] At 301.22 K.

TABLE 3
Experimental values of density (ρ), dynamic viscosity (η), surface tension (σ) of ILs at several temperatures and calculated values of thermal expansion coefficients (α_p) using equation (5)

T/K	ρ/(g · cm^{-3})	η^a/(MPa · s)	σ/(mN · m^{-1})	$\alpha_p \cdot 10^{-5}$/K^{-1}
		[C$_6$mim][BF$_4$]		
288.15		141		
298.15	1.14532	102	36.8	7.42619
308.15	1.13851	69	35.6	7.42619
318.15	1.13167	43	34.2	7.42618
328.15	1.12489	30	33.0	7.42618
338.15	1.11816	21	32.7	7.42618
348.15	1.11147			7.42617
358.15	1.10484			7.42617
		[C$_6$mim][PF$_6$]		
288.15		1018		
298.15	1.29341	607	42.1	6.55063
308.15	1.28578	345	40.7	6.55063
318.15	1.27792	215	39.4	6.55062
328.15	1.26988	152	38.0	6.55062
338.15	1.26213	113	36.6	6.55062
348.15	1.25436	87		6.55061
358.15	1.24681			6.55061
		[C$_6$mim][Tf$_2$N]		
288.15		97		
298.15	1.37213	68	32.5	6.09783
308.15	1.36317	46	31.6	6.09780
318.15	1.35423	32	30.5	6.09776
328.15	1.34494	24	29.7	6.09773
338.15	1.33586		28.6	6.09769
348.15	1.32691			6.09766
358.15	1.31816			6.09763

[a] At temperatures (288.2, 298.2, 308.2, 318.2, 328.2, 338.2, 348.2) K.

The experimental data for all the measured physical properties is presented by the following general equations:

$$Z = A_0 + A_1 T, \tag{1}$$

$$\lg \eta = A_0 + A_1/T \tag{2}$$

and

$$\sigma = A_0 + A_1/T, \tag{3}$$

where $Z = \rho$ or n_D, T is the temperature, and A_0 and A_1 are correlation coefficients. The values of A_0 and A_1 are estimated using a method of least square fitting for equations (1) to (3) and are presented in table 5 along with the standard deviation (SD) values calculated using the following expression:
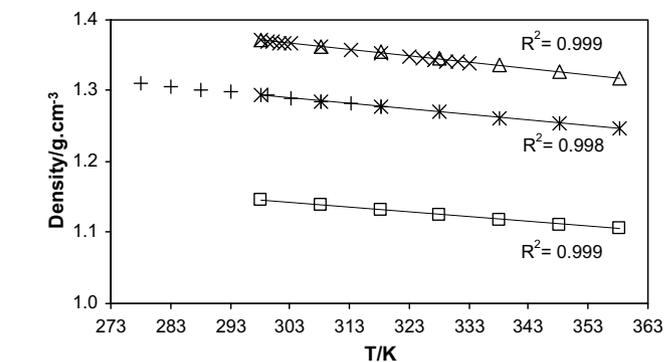
FIGURE 1. Plot of experimental ρ values against T for □, [C$_6$mim][BF$_4$]; *, [C$_6$mim][PF$_6$]; △, [C$_6$mim][Tf$_2$N]: this work with fitted curves and +, [C$_6$mim][PF$_6$] by Pereiro et al. [11]; ×, [C$_6$mim][Tf$_2$N] by Gomes de Azevedo et al. [19].
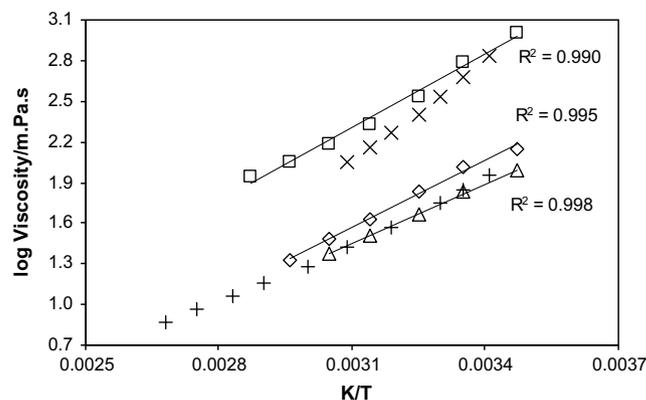
FIGURE 2. Plot of lg η values against $1/T$ for □, [C$_6$mim][PF$_6$]; ◇, [C$_6$mim][BF$_4$]; △, [C$_6$mim][Tf$_2$N]: this work with fitted curves and ×, [C$_6$mim][PF$_6$] by Pereiro et al. [4]; +, [C$_6$mim][Tf$_2$N] by Widegren and Magee [23].

$$\text{SD} = \sqrt{\sum_i^{n_{DAT}} (Z_{exp} - Z_{cal})2/n_{DAT}}, \tag{4}$$

where n_{DAT} is the number of experimental points, Z_{exp} and Z_{cal} are experimental and calculated data values, respectively. The coefficients of thermal expansion values for [C$_6$mim][BF$_4$], [C$_6$mim][PF$_6$]
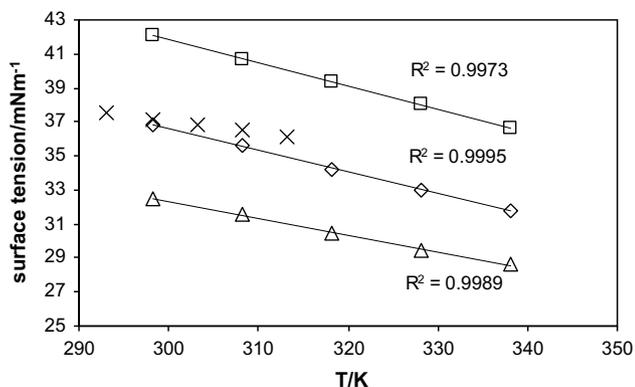
FIGURE 3. Plot of experimental σ values against T for □, [C$_6$mim][PF$_6$]; ◇, [C$_6$mim][BF$_4$]; △, [C$_6$mim][Tf$_2$N]: this work with fitted curves and ×, [C$_6$mim][PF$_6$] by Pereiro et al. [4].

TABLE 5
Fitting parameters of equations (1) to (3) to correlate physical properties of ILs and standard deviations (SD) using equation (4)

Physical properties	A_0	A_1	SD
	[C$_6$mim][BF$_4$]		
$\rho/(g \cdot cm^{-3})$	1.3467	−0.0002	0.222
$\lg \eta/(MPa \cdot s)$	−3.5499	1651.1	0.01
$\sigma/mN\ m^{-1}$	−6.1919	12,848	0.06
n_D	1.4814	−0.0001	0.057
	[C$_6$mim][PF$_6$]		
$\rho/(g \cdot cm^{-3})$	1.5267	−0.0001	0.257
$\lg \eta/(MPa \cdot s)$	−3.3107	1811.4	0.03
$\sigma/mN\ m^{-1}$	−4.5828	13,950	0.09
n_D	1.4645	−0.0001	0.05
	[C$_6$mim][Tf$_2$N]		
$\rho/(g \cdot cm^{-3})$	1.6413	−0.0001	0.297
$\lg \eta/(MPa \cdot s)$	−3.1333	1477.7	0.006
$\sigma/mN\ m^{-1}$	−1.2547	10,094	0.06
n_D	1.4868	−0.0001	0.06

TABLE 4
Refractive indices, n_D of ILs at temperatures (302.95–332.95) K

T/K	[C$_6$mim][BF$_4$]	[C$_6$mim][PF$_6$]	[C$_6$mim][Tf$_2$N]
302.95	1.42672	1.41694	1.42958
307.75	1.42613	1.41631	1.42844
313.15	1.42539	1.41531	1.42737
318.05	1.42443	1.41479	1.42649
322.95	1.42346	1.41362	1.42578
328.05	1.42232	1.41307	1.42484
332.95	1.42146	1.41231	1.42376

TABLE 6
Thermal decomposition values of ILs in this work and literature

	T_{start} (°C)		T_{onset} (°C)	
	10/(°C · min^{-1})	20/(°C · min^{-1})	10/(°C · min^{-1})	20/(°C · min^{-1})
[C$_6$mim][BF$_4$]	262	239	425	426
[C$_6$mim][PF$_6$]	320	289	454	446
			417[a] [14]	
[C$_6$mim][Tf$_2$N]	302	282	461	417
			428 [18]	

[a] With water contents = 472 ppm.
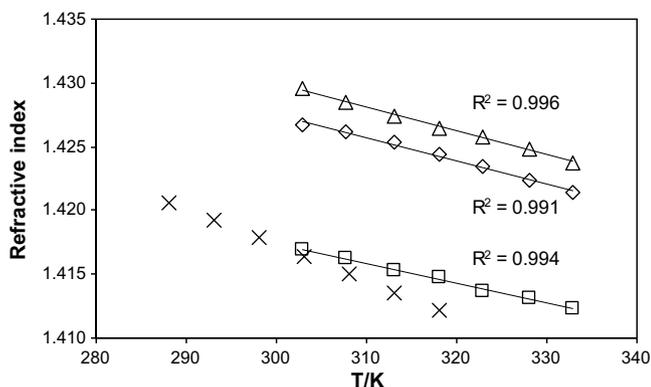
FIGURE 4. Experimental n_D values against T for △, [C$_6$mim][Tf$_2$N]; ◇, [C$_6$mim][BF$_4$]; □, [C$_6$mim][PF$_6$]: this work with fitted curves and ×, [C$_6$mim][PF$_6$] by Pereiro et al. [11].

and [C$_6$mim][Tf$_2$N] are calculated from the experimental density data of respective IL using the following equation:

$$\alpha_p Z = -1/\rho \cdot (\partial\rho/\partial T)_p = -(A_1)/(A_0 + A_1 T), \qquad (5)$$

where α_p is the coefficient of thermal expansion, ρ is the density of IL, T is the temperature and A_0 and A_1 are correlation coefficients taken from equation (1) by fitting density data. It can be observed from table 3 that the coefficients of thermal expansion of each IL do not change considerably. Thus, the variation of volume expansion of ILs studied in the present work could be considered as independent of temperature which is in good agreement with the reported observation of Pereiro et al. [4] for [C$_4$mim][PF$_6$] and [C$_8$mim][PF$_6$].

Thermal decomposition values of ILs are reported in terms of start temperature (T_{start}) and onset temperature (T_{onset}) in table 6 at two different heating rates (10 and 20) °C · min^{-1} together with the literature values. The sample plots of thermal decomposition of ILs at heating rate of 10 °C · min^{-1} are shown in figure 5.

The temperature at which the decomposition of the sample just begins is known as T_{start} whereas T_{onset} is the intersection of the baseline weight and the tangent of the weight vs temperature curve as the decomposition occurs. The rates of heating in this work, i.e., (10 and 20) °C · min^{-1} have not significantly affected the thermal decomposition values of ILs. However, all the ILs have lower start decomposition temperature at heating rate of 20 °C · min^{-1} as compared to 10 °C · min^{-1}. A small shoulder near the minimum of thermogram derivative in figure 5b and c was also observed, which could be due to the short time lag in real-time calculations between the sample and furnace temperatures and the dependence of weight loss rate on the morphology of the particular sample or due to the difference in energy released/absorbed via chemical reactions during heating process.

5. Conclusion

In the present work, physical properties such as density, dynamic viscosity, surface tension, and refractive indices of three ILs (vacuum dried) are investigated at several temperatures and reported along with their characterization data in terms of chloride and water contents. Thermophysical properties of ILs are, by no means extensive in the open literature, particularly for [C$_6$mim][BF$_4$] and [C$_6$mim][Tf$_2$N]. The fitting of experimental values are performed by the least square regression technique
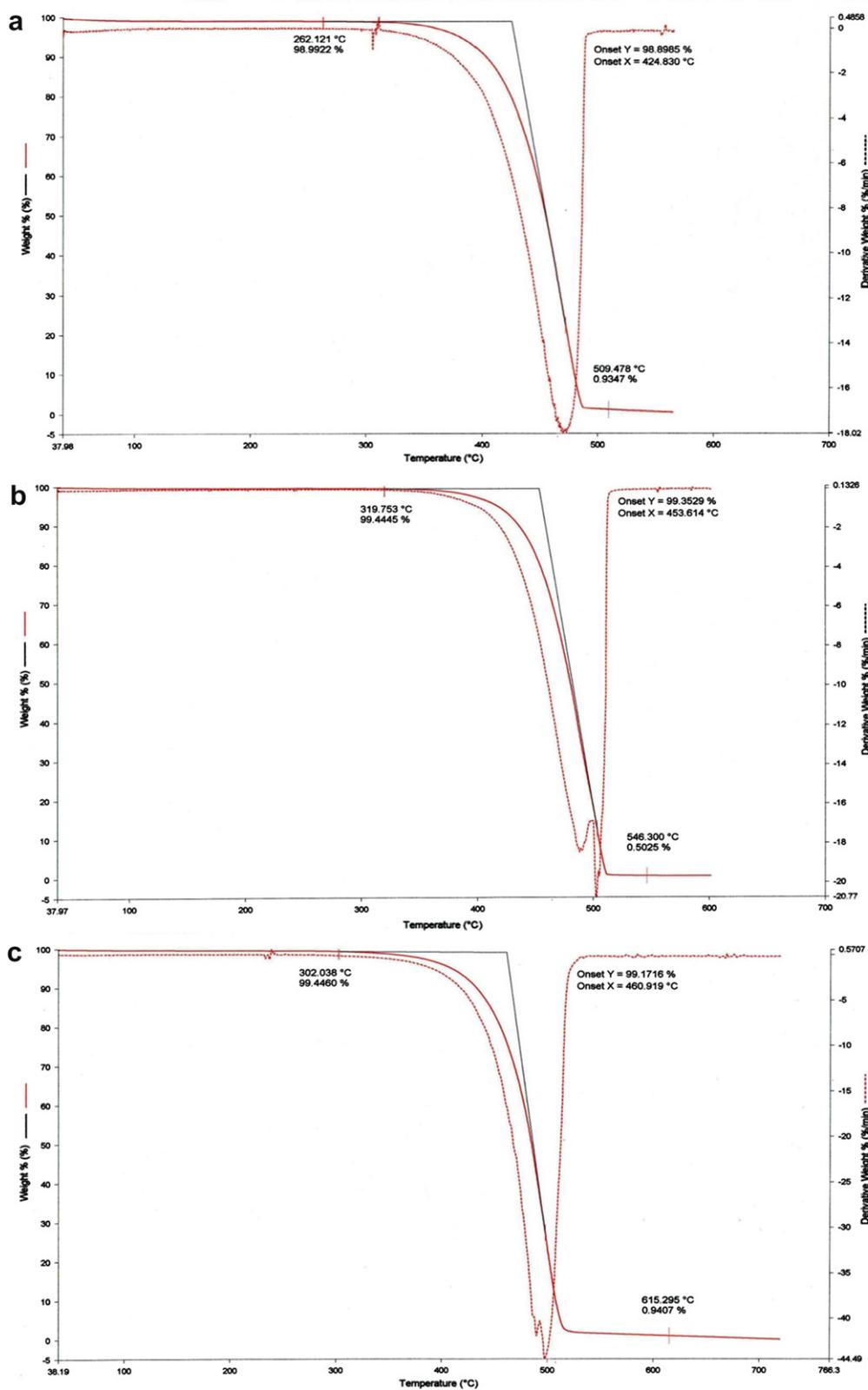
FIGURE 5. Plot of thermal decomposition of [C_6mim][BF_4] (a), [C_6mim][PF_6] (b) and [C_6mim][Tf_2N] (c) at heating rate of 10 °C · min^{-1}.

using empirical correlations. The coefficients of thermal expansion of ILs studied here are calculated using experimental density data to evaluate the effect of temperature on the variation of volume expansion. The type of anion plays a crucial role in thermal decomposition of ILs, which is evident from the values of thermal stability, found to increase in 1-hexyl-3-methyl imidazolium based ILs in order of $Tf_2N > PF_6 > BF_4$ anions.

References

[1] J.S. Wilkes, J. Mol. Catal. A: Chem. 214 (2004) 11–17.
[2] H. Xue, R. Verma, J.M. Shreeve, J. Fluorine Chem. 127 (2006) 159–176.
[3] C.P. Fredlake, J.M. Crosthwaite, D.G. Hert, S.N.V.K. Aki, J.F. Brennecke, J. Chem. Eng. Data 49 (2004) 954–964.
[4] A.B. Pereiro, J.L. Legido, A. Rodrı'guez, J. Chem. Thermodyn. 39 (2007) 1168–1175.
[5] J. Kumełan, A.P.S. Kamps, D. Tuma, G. Maurer, J. Chem. Thermodyn. 38 (2006) 1396–1401.
[6] D. Camper, P. Scovazzo, C. Koval, R. Noble, Ind. Eng. Chem. Res. 43 (2004) 3049–3054.
[7] R.P. Swatloski, J.D. Rogers, R.D. Rogers, Green Chem. 5 (2003) 361–363.
[8] V. Najdanovic-Visak, J.M.S.S. Esperanca, L.P.N. Rebelo, M. Nunes da Ponte, H.J.R. Guedes, K.R. Seddon, J. Szydlowski, Phys. Chem. Phys. 4 (2002) 1701–1703.
[9] A.E. Visser, R.P. Swatloski, W.M. Reichert, S.T. Griffin, R.D. Rogers, Ind. Eng. Chem. Res. 39 (2000) 3596–3604.
[10] K.R. Seddon, A. Stark, M.J. Torres, Pure Appl. Chem. 72 (12) (2000) 2275–2287.
[11] A.B. Pereiro, E. Tojo, A. Rodrı'guez, J. Canosa, J. Tojo, J. Chem. Thermodyn. 38 (2006) 651–661.
[12] J. Wang, Y. Tian, Y. Zhao, K. Zhuo, Green Chem. 5 (2003) 618–622.
[13] G. Law, P.R. Watson, Langmuir 17 (2001) 6138–6141.
[14] J.G. Huddleston, A.E. Visser, W.M. Reickert, H.D. Willauer, G.A. Broker, R.D. Rogers, Green Chem. 3 (2001) 156–169.
[15] K.R. Seddon, A. Stark, M.J. Torres, ACS Symp. Ser. 819 (2002) 34–49.
[16] T.M. Letcher, P. Reddy, J. Chem. Thermodyn. 37 (2005) 415–421.
[17] J. Liu, G.B. Jiang, Y. Chi, Y. Cai, Q. Zhou, J. Hu, Anal. Chem. 75 (2003) 58–70.
[18] H. Tokuda, K. Hayamizu, K. Ishii, M.A.B.H. Susan, M. Watanabe, J. Phys. Chem. B 109 (2005) 6103–6110.
[19] R. Gomes de Azevedo, J.M.S.S. Esperanca, J. Szydlowski, Z.P. Visak, P.F. Pires, H.J.R. Guedes, L.P.N. Rebelo, J. Chem. Thermodyn. 37 (2005) 888–899.
[20] K.S. Kim, B.K. Shin, H. Lee, Korean J. Chem. Eng. 21 (2004) 1010–1014.
[21] S.V. Dzyuba, R.A. Bartsch, Chem. Phys. Chem. 3 (2002) 161–166.
[22] P. Kilaru, G.A. Baker, P. Scovazzo, J. Chem. Eng. Data 52 (2007) 2306–2314.
[23] J.A. Widegren, J.W. Magee, J. Chem. Eng. Data 52 (2007) 2331–2338.

JCT 07-319