J. Chem. Eng. Data **2010,** *55,* 4928–4930

Density and Surface Tension of Ionic Liquids [C$_n$py][NTf$_2$] (n = 2, 4, 5)

Qing-Shan Liu,[†] Miao Yang,[†] Pei-Fang Yan,[†] Xiu-Mei Liu,[†] Zhi-Cheng Tan,*[,†,‡] and Urs Welz-Biermann*[,†]

China Ionic Liquid Laboratory, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China, and Thermochemistry Laboratory, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

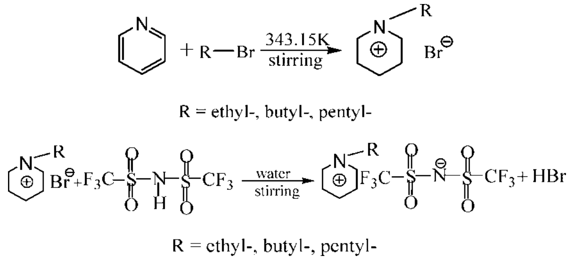
Density and surface tension of the air- and water-stable hydrophobic ionic liquids *N*-alkylpyridinium bis(trifluoromethylsulfonyl)imide ([C$_n$py][NTf$_2$], n = 2, 4, 5) were measured in the temperature range T = (283.15 to 338.15) K. The melting temperatures of the samples were determined by differential scanning calorimetry (DSC). Decomposition temperatures are higher than 600 K as determined by thermogravimetric analysis (TG).

Introduction

Ionic liquids (ILs) as organic salts have exhibited low melting temperature, good solvation, nonvolatility properties, and higher thermodynamic stability, so both industrial and scientific communities are advertising them for broad ranges of applications as green solvents. Actually, most ILs are hydrophilic; therefore, the anions for hexafluorophosphate (PF_6^-) and bis(trifluoromethylsulfonyl)imide (NTf_2^-) ILs attracted much concern as hydrophobic compounds when they appeared,[1−4] and the properties were reporting in succession when the hydrophobic compounds were synthesized.[5−11] In this paper, the authors synthesized three pyridinium ILs, which are also the air- and water-stable hydrophobic compounds. The study of the properties of these three ILs is significant in many concerned fields.

Experimental Section

Preparation of ILs ([C$_n$py][NTf$_2$], n = 2, 4, 5). *N*-Alkylpyridinium bromide ([C$_n$py][Br] n = 2, 4, 5) was synthesized according to the procedure described in an earlier paper.[12] [C$_2$py][NTf$_2$], [C$_4$py][NTf$_2$], and [C$_5$py][NTf$_2$] were synthesized according to the ion exchange reaction, where 80 g of [C$_n$py][Br] (n = 2, 4, 5) was placed in a 500 mL round-bottomed flask and dissolved in 30 mL of distilled water. Then, the equivalent amount of bis(trifluoromethanesulfonyl)imide ($HN(SO_2CF_3)_2$ donated by Rhodia Co.) was added dropwise into the flask at room temperature and stirred for 3 h. The purity of $HN(SO_2CF_3)_2$ is 99.9 % by mass which was dissolved in the distilled water, and the mass fraction of the aqueous solution is 70 %. The lower liquid was washed several times with 30 mL of distilled water until no Br^- was indicated by the solution of $AgNO_3/HNO_3$. The final product was dried under the vacuum at 353 K for 24 h. ^{1}H and ^{13}C NMR spectra were recorded (see Figures S1, S2, S3, S4, S5, S6, S7, and S8 and Tables S1, S2, and S3 in the Supporting Information) except those for [C$_2$py][Br].[12] From the NMR, impurity peaks were not found. The reaction equations are following:



R = ethyl-, butyl-, pentyl-

R = ethyl-, butyl-, pentyl-

Measurement of DSC and TG. Differential scanning calorimetry (DSC) was carried out on a Q2000 V24.4 Build 116 at a heating rate of 10 K$\cdot$min^{-1} under a nitrogen atmosphere over a temperature range of (153 to 413) K. The data of the thermal properties of the three compounds are listed in Table 1.

The decomposition temperature of the ILs was determined on a Netzsch TG 209 at a heating rate of 10 K$\cdot$min^{-1} under a nitrogen atmosphere over a temperature range of (313 to 823) K (see Figure S9 of DSC and TG). The percent of the mass loss at different temperatures is listed in Table 2.

Measurement of Density and Surface Tension. The density (ρ/g$\cdot$cm^{-3}) and surface tension (γ/mJ$\cdot$m^{-2}) were measured at atmospheric pressure. Since the trace water still exists in the ILs after drying by common methods, the presence of water becomes the most problematic impurity and needs to be confirmed before and after measurement. The mass fraction of water is the average of three measurements carried out by a Cou-Lo Aquamax Karl Fischer Moisture Meter (v.10.06) and is listed in Table 3.

The densities of degassed water were measured by a Westphal balance. The results are in good agreement with the literature values,[13] and the uncertainty is ± 0.0002 g$\cdot$cm^{-3}. Then, the densities of the samples were measured in the temperature range of T = (283.15 to 338.15) K. The sample was placed in a cell with a jacket. The density values were recorded at per 5 K intervals. The temperature was controlled by a thermostat with an uncertainty of ± 0.05 K. Each data point of the density is the average value of three measurements. The results are listed in Table 4.

Using the tensiometer (DP-AW type produced by Sang Li Electronic Co.) of the forced bubble method, the surface tension of the double-distilled freshly degassed water was measured in the range of T = (283.15 to 338.15) K, which is in good agreement with the literature,[13] and the uncertainty is ± 0.1 mJ$\cdot$m^{-2}. The temperature was controlled by a thermostat with an uncertainty of ± 0.05 K. The surface tension of the sample

---

* Corresponding authors. E-mail: tzc@dicp.ac.cn (Zhi-Cheng Tan) and uwb@dicp.ac.cn (Urs Welz-Biermann).

[†] China Ionic Liquid Laboratory.

[‡] Thermochemistry Laboratory.

10.1021/je100507n © 2010 American Chemical Society
Published on Web 09/09/2010

Table 1. Molecular Weight and Thermal Properties from the DSC

	MW	T_g	T_m	ΔH_m	ΔS_m
	g·mol^{-1}	K	K	kJ·mol^{-1}	J·K^{-1}·mol^{-1}
[C_2py][NTf_2]	388.30	235.24 ± 0.01	303.65 ± 0.01	18.9 ± 0.2	62.2 ± 0.2
[C_4py][NTf_2]	416.35		299.05 ± 0.01	27.9 ± 0.3	93.2 ± 0.3
[C_5py][NTf_2]	430.38	196.22 ± 0.01	272.84 ± 0.01	22.8 ± 0.2	83.6 ± 0.2

Table 2. Mass Loss of the ILs [C_2py][NTf_2], [C_4py][NTf_2], and [C_5py][NTf_2] Following the Temperature Recorded by TG

	T/K		
100 δ_m/m	[C_2py][NTf_2]	[C_4py][NTf_2]	[C_5py][NTf_2]
1.93			611.45 ± 0.1[a]
3.04		611.85 ± 0.1[a]	
3.49	585.55 ± 0.1[a]		
5	608.65 ± 0.1	632.35 ± 0.1	636.75 ± 0.1
10	635.65 ± 0.1	651.35 ± 0.1	650.75 ± 0.1
20	656.65 ± 0.1	666.35 ± 0.1	664.75 ± 0.1
50	678.65 ± 0.1	685.35 ± 0.1	683.75 ± 0.1
80	695.65 ± 0.1	700.35 ± 0.1	697.75 ± 0.1
90	713.65 ± 0.1	707.35 ± 0.1	702.75 ± 0.1
7.88	723.05 ± 0.1[b]		
1.57			710.85 ± 0.1[b]
0.70		721.35 ± 0.1[b]	

[a] The onset temperature. [b] The terminal temperature, respectively.

Table 3. Mass Fraction of Water before and after the Measurement of Density and Surface Tension

	density		surface tension	
10^4 w	before	after	before	after
[C_2py][NTf_2]	3.32	7.70	5.03	6.32
[C_4py][NTf_2]	6.11	8.91	8.82	9.05
[C_5py][NTf_2]	1.66	4.20	6.14	6.83

was measured with the same method. Each data point of the surface tension is the average value of five measurements. The results of the surface tension of the samples are listed in Table 4.

Result and Discussion

The molecular weights of the three compounds are listed in Table 1. The glass temperature (T_g), crystallization temperature (T_c), and melting temperature (T_m) can be obtained from the DSC thermograms during the programmed heat/cool/heat step. From the DSC, the melting temperature of the three samples decreases with the increase of methylene. There are two endothermic peaks for [C_2py][NTf_2], which indicated that it probably has the transition from solid to solid at 292.80 K and melting at 303.65 K. There are two exothermic peaks for [C_5py][NTf_2] at (234.98 and 256.36) K, which indicated that it has two crystal forms.

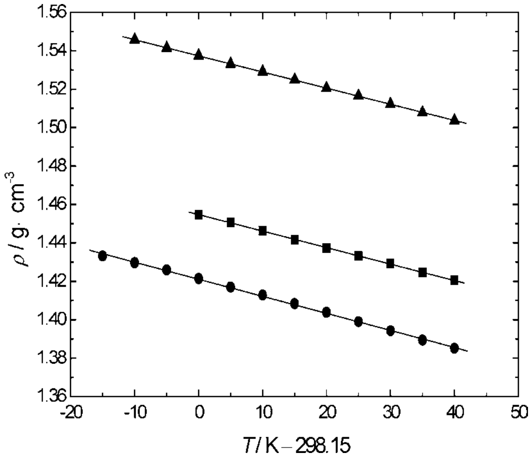


Figure 1. Plot of ρ vs (T/K − 298.15): ▲, [C_2py][NTf_2]; ■, [C_4py][NTf_2]; ●, [C_5py][NTf_2].

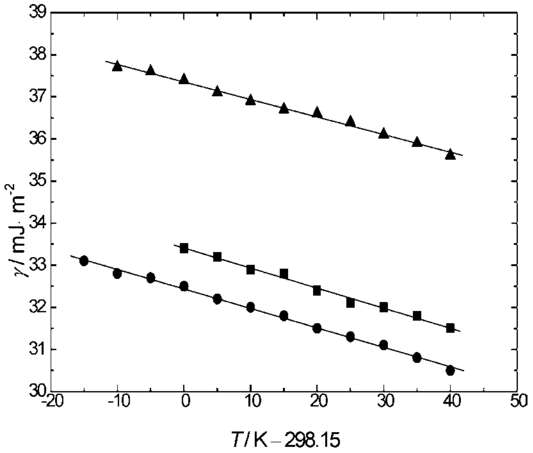


Figure 2. Plot of γ vs (T/K − 298.15): ▲, [C_2py][NTf_2]; ■, [C_4py][NTf_2]; ●, [C_5py][NTf_2].

From the TG, the decomposition temperature of the three ILs is higher than 600.0 K. The samples exhibited excellent thermal stability up to 600.0 K at the scanning rate of 10 K·min^{-1}; the mass loss of the three ILs is more than 90 % from the onset temperature to the terminal temperature. The onset temperature of mass loss decreased with increasing methylene.

The values of ρ and γ for the three ILs decreased with increasing temperature as shown in Figures 1 and 2. The experimental data were correlated with the following equation

Table 4. Experimental Values of Density, ρ, and Surface Tension, γ, of ILs [C_2py][NTf_2], [C_4py][NTf_2], and [C_5py][NTf_2]

	[C_2py][NTf_2]		[C_4py][NTf_2]		[C_5py][NTf_2]	
T	ρ	γ	ρ	γ	ρ	γ
K	g·cm^{-3}	mJ·m^{-2}	g·cm^{-3}	mJ·m^{-2}	g·cm^{-3}	mJ·m^{-2}
283.15					1.4331 ± 0.0002	33.1 ± 0.1
288.15	1.5457 ± 0.0002	37.7 ± 0.1			1.4296 ± 0.0002	32.8 ± 0.1
293.15	1.5414 ± 0.0002	37.6 ± 0.1			1.4259 ± 0.0002	32.7 ± 0.1
298.15	1.5375 ± 0.0002	37.4 ± 0.1	1.4547 ± 0.0002	33.4 ± 0.1	1.4214 ± 0.0002	32.5 ± 0.1
303.15	1.5332 ± 0.0002	37.1 ± 0.1	1.4506 ± 0.0002	33.2 ± 0.1	1.4169 ± 0.0002	32.2 ± 0.1
308.15	1.5291 ± 0.0001	36.9 ± 0.1	1.4462 ± 0.0001	32.9 ± 0.1	1.4128 ± 0.0001	32.0 ± 0.1
313.15	1.5249 ± 0.0001	36.7 ± 0.1	1.4417 ± 0.0001	32.8 ± 0.1	1.4083 ± 0.0001	31.8 ± 0.1
318.15	1.5205 ± 0.0001	36.6 ± 0.1	1.4372 ± 0.0001	32.4 ± 0.1	1.4038 ± 0.0001	31.5 ± 0.1
323.15	1.5164 ± 0.0001	36.4 ± 0.1	1.4332 ± 0.0001	32.1 ± 0.1	1.3989 ± 0.0001	31.3 ± 0.1
328.15	1.5122 ± 0.0001	36.1 ± 0.1	1.4291 ± 0.0001	32.0 ± 0.1	1.3942 ± 0.0001	31.1 ± 0.1
333.15	1.5078 ± 0.0001	35.9 ± 0.1	1.4245 ± 0.0001	31.8 ± 0.1	1.3893 ± 0.0001	30.8 ± 0.1
338.15	1.5037 ± 0.0001	35.6 ± 0.1	1.4205 ± 0.0001	31.5 ± 0.1	1.3851 ± 0.0001	30.5 ± 0.1

Table 5. Fitting Parameters and Standard Deviations for the ρ and γ of ILs [C_2py][NTf_2], [C_4py][NTf_2], and [C_5py][NTf_2]

	ρ/g·cm^{-3}			γ/mJ·m^{-2}		
ILs	10^4A	B	s	10^3A	B	s
[C_2py][NTf_2]	8.40	1.5374	0.0001	41.6	37.4	0.0619
[C_4py][NTf_2]	8.59	1.4547	0.0002	47.7	33.4	0.0698
[C_5py][NTf_2]	8.87	1.4210	0.0006	46.2	32.4	0.0554

$$Y = B - A \cdot (T/\mathrm{K} - 298.15) \qquad (1)$$

where Y are ρ/g·cm^{-3} and γ/mJ·m^{-2}; A and B are adjustable parameters. The fitting parameters and standard deviations are listed in Table 5.

According to the Auerbach relation,[14] the speed of sound can be calculated from the density and surface tension by the following equation

$$u/\mathrm{m \cdot s^{-1}} = (\gamma/(0.00063\rho))^{2/3} \qquad (2)$$

where γ is surface tension; ρ is density; and u is speed of sound. The estimated values at 298.15 K for the three compounds are listed in Table S4 (Supporting Information).

The physicochemical properties (molecular volume, V_m, parachor, P, thermal expansion coefficient, α, standard entropy, S^0, lattice energy, U_{pot}, and molar enthalpy of vaporization, $\Delta_l^g H_m^0$) were estimated by using the experimental data of density and surface tension. The process of the estimation has been described in previous papers.[15−17] These estimated values are listed in Table S4 (Supporting Information).

From Table S4 (Supporting Information), the molecular volume, V_m, standard entropy, S^0, and parachor, P, are plotted against the number of the carbons, n, in the alkyl chain of the samples ([$C_n$py][NTf_2], $n = 2, 4, 5$) and shown in Figures S10 and S11 (Supporting Information).

From the Figures S10 and S11 (Supporting Information), the contribution per methylene ($-CH_2-$) group to the molecular volume, standard entropy, and parachor was found to be 0.0278 nm^3, 34.7 J·K^{-1}·mol^{-1}, and 32.7. The values of 0.0278 nm^3 and 34.7 J·K^{-1}·mol^{-1} are in good agreement with the literature values of 0.0272 nm^3 and 33.9 J·K^{-1}·mol^{-1} for [$C_n$mim][BF_4],[18] 0.0282 nm^3 and 35.1 J·K^{-1}·mol^{-1} for [$C_n$mim][NTf_2],[18] 0.0270 nm^3 and 34.6 J·K^{-1}·mol^{-1} for [$C_n$mim][$AlCl_4$],[15] and 0.0278 nm^3 and 33.7 J·K^{-1}·mol^{-1} for [$C_n$mim][Ala].[19] The value of 32.7 is similar to the value of 31.1 for [$C_n$mim][$AlCl_4$][15] but much less than the value of 37.5 for [$C_n$mim][Ala][19] and 39.9 for the neutral parachor contribution values of methylene.[20]

Conclusions

Density and surface tension of [$C_n$py][NTf_2] ($n = 2, 4, 5$) were experimentally measured. The order of the density and surface tension is [C_2py][NTf_2] > [C_4py][NTf_2] > [C_5py][NTf_2], at 298.15 K. The order of melting point is [C_2py][NTf_2] (303.65 K) > [C_4py][NTf_2] (299.05 K) > [C_5py][NTf_2] (273.44 K), according to differential scanning calorimetry. They exhibited higher thermal stability up to 600.0 K from the thermogravimetric analysis.

Supporting Information Available:

Additional experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Fuller, J.; Carlin, R. T.; Long, H. C. D.; Haworth, D. Structure of 1-ethyl-3-methylimidazolium hexafluorophosphate: model for room temperature molten salts. *J. Chem. Soc., Chem. Commun.* **1994**, 299–300.

(2) Gordon, C. M.; Holbrey, J. D.; Kennedy, R.; Seddon, K. R. Ionic liquid crystals: hexafluoroposphate salts. *J. Mater. Chem.* **1998**, *8*, 2627–2636.

(3) Bonhôte, P.; Dias, A. P.; Papageorgiou, N.; Kalyanasundaram, K.; Grätzel, M. Hydrophobic, highly comductive ambient-temperature molten salts. *Inorg. Chem.* **1996**, *35*, 1168–1178.

(4) Cammarata, L.; Kazarian, S. G.; Salter, P. A.; Welton, T. Molecular states of water in room temperature ionic liquids. *Phys. Chem. Chem. Phys.* **2001**, *3*, 5192–5200.

(5) Restolho, J.; Serro, A. P.; Mata, J. L.; Saramago, B. Viscosity and surface tension of 1-ethanol-3-methylimidazolium tetrafluoroborate and 1-methyl-3-octylimidazolium tetrafluoroborate over a wide temperature range. *J. Chem. Eng. Data* **2009**, *54*, 950–955.

(6) kabo, G. J.; blokhin, A. V.; Paulechka, Y. U.; Kabo, A. G.; Shymanovich, M. P.; Magee, J. W. Thermodynamic properties of 1-butyl-3-methylimidazolium hexafluorophosphate in the condensed state. *J. Chem. Eng. Data* **2004**, *49*, 453–461.

(7) Fredlake, C. P.; Crosthwaite, J. M.; Hert, D. G.; Aki, S. N. V. K.; Brennecke, J. F. Thermophysical properties of imicazolium-based ionic liquids. *J. Chem. Eng. Data* **2004**, *49*, 954–961.

(8) Harris, K. R.; Woolf, L. A.; Kanakubo, M. Temperature and pressure dependence of the viscosity of the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate. *J. Chem. Eng. Data* **2005**, *50*, 1777–1782.

(9) Anthony, J. L.; Maginn, E. J.; Brennecke, J. F. Solubilities and thermodynamic properties of gases in the ionic liquid 1-*n*-butyl-3-methylimizazolium hexafluorophosphate. *J. Phys. Chem. B* **2002**, *106*, 7315–7320.

(10) Tokuda, H.; Hayamizu, K.; Ishii, K.; Susan, M. A. B. H.; Watanabe, M. Physicochemical properties and structures of room temperature ionic liquids. 1. Variation of anionic species. *J. Phys. Chem. B* **2004**, *108*, 16593–16600.

(11) Tokuda, H.; Hayamizu, K.; Ishii, K.; Susan, M. A. B. H.; Watanabe, M. Physicochemical properties and structures of room temperature ionic liquids. 2. Variation of alkyl chain length in imidazolium cation. *J. Phys. Chem. B* **2005**, *109*, 6103–6110.

(12) Tong, B.; Liu, Q. S.; Tan, Z. C.; Welz-Biermann, U. Thermochemistry of alkyl pyridinium bromide ionic liquids: Calorimetric measurements and calculations. *J. Phys. Chem. A* **2010**, *114*, 3782–3787.

(13) Lide, D. R. *Handbook of Chemistry and Physics*, 82nd ed.; CRC Press: Boca Raton, 2001−2002.

(14) Bandrés, I.; Giner, B.; Artigas, H.; Royo, F. M.; Lafuente, C. Thermophysic comparative study of two isomeric pyridinium-based ionic liquids. *J. Phys. Chem. B* **2008**, *112*, 3077–3084.

(15) Tong, J.; Liu, Q. S.; Xu, W. G.; Fang, D. W.; Yang, J. Z. Estimation of physicochemical properties of ionic liquids 1-alkyl-3-methylimidazolium chloroaluminate. *J. Phys. Chem. B* **2008**, *112*, 4381–4386.

(16) Tong, J.; Liu, Q. S.; Guan, W.; Yang, J. Z. Estimation of physicochemical properties of ionic liquid $C_6MIGaCl_4$ using surface tension and density. *J. Phys. Chem. B* **2007**, *111*, 3197–3200.

(17) Liu, Q. S.; Tong, J.; Tan, Z. C.; Welz-Biermann, U.; Yang, J. Z. Density and surface tension of ionic liquid [C_2mim][$PF_3(CF_2CF_3)_3$] and prediction of properties [$C_n$mim][$PF_3(CF_2CF_3)_3$] ($n = 1, 3, 4, 5, 6$). *J. Chem. Eng. Data* **2010**, *55*, 2586–2589.

(18) Glasser, L. Lattice and phase transition thermodynamics of ionic liquids. *Thermochim. Acta* **2004**, *421*, 87–93.

(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. B* **2008**, *112* (25), 7499–7505.

(20) Knotts, T. A.; Wilding, W. V.; Oscarson, J. L.; Rowley, R. L. Use of the DIPPR database for development of QSPR correlations: Surface Tension. *J. Chem. Eng. Data* **2001**, *46*, 1007–1012.

Received for review May 14, 2010. Accepted August 18, 2010. Funding for this research was provided by the National Natural Science Foundation of China (NSFC No. 20901076) and Knowledge Innovation Program of the Chinese Academy of Science, DICP (Grant K2009D03).

JE100507N