

Physicochemical properties of phosphonium-based and ammonium-based protic ionic liquids†

Jiangshui Luo,^{ab} Olaf Conrad^{*c} and Ivo F. J. Vankelecom^{*a}

Received 4th July 2012, Accepted 6th August 2012

DOI: 10.1039/c2jm34359b

Trioctylphosphonium triflate, trioctylammonium triflate, triphenylphosphonium triflate and triphenylammonium triflate were synthesized and characterized. It was found that phosphonium-based protic ionic liquids (PILs) exhibit higher thermal stability and ionic conductivity than the corresponding ammonium-based PILs, no matter whether the P and N center atoms are bonded to the electron-donating octyl groups or the electron-withdrawing phenyl groups. The ion conduction behavior of the PILs can be adequately described by the Vogel–Fulcher–Tamman (VFT) equation. The higher ionic conductivity of phosphonium-based PILs may be attributed to their weaker hydrogen bond and Coulombic interactions as well as higher carrier ion concentrations, indicated by infrared analysis, lattice potential energy estimation and VFT fitting results. Interestingly, the stronger hydrogen bonds inside trioctylammonium triflate may lead to a much decreased melting point. Furthermore, compared with electron-withdrawing phenyl, electron-donating octyl enhanced the thermal stability of the PILs.

1. Introduction

Ionic liquids include subgroups of protic (PILs) and aprotic ionic liquids (AILs).^{1,2} PILs are formed by the stoichiometric combination of a Brønsted acid and a Brønsted base, while AILs are formed by transfer of an alkyl group (or a group of comparable complexity) to the same site occupied by a proton in a PIL.³ So far, AILs have received much more attention than PILs. Nevertheless, due to their protic nature, PILs have been intensively studied as proton-conducting electrolytes in various fields such as fuel cells and supercapacitors.^{1–11} Indeed, the key property that distinguishes PILs from AILs is the proton transfer from the acid to the base, leading to the presence of proton-donor and proton-acceptor sites, which can be used to build up a hydrogen-bonded network.^{12,13}

Phosphonium-based AILs are of considerable interest with regard to electrochemical aspects and have been reported to be superior to their ammonium counterparts in terms of thermal stability, viscosity, ionic conductivity and electrochemical

stability.^{14–20} For example, Tsunashima and Sugiya¹⁶ reported that AILs based on triethylalkylphosphonium cations and the $N(SO_2CF_3)_2^-$ anion showed excellent electrochemical and thermal stabilities as well as quite low viscosities, when compared with the corresponding ammonium AILs.

However, while a great deal of attention has been given to ammonium-based PILs, phosphonium-based PILs have received far less attention as electrolytes,^{11,21,22} although they have found some applications in catalysis.^{23–25} Recently, Rana *et al.*²¹ showed that PILs based on a tributylphosphonium cation exhibit higher acidities, thermal stabilities and conductivities as well as lower viscosities over the corresponding ammonium analogues. In addition, Anouti *et al.* used a solution of tributylphosphonium tetrafluoroborate in acetonitrile as an electrolyte for carbon-based supercapacitors, which showed capacities comparable to conventional aqueous electrolytes and a combination of good cycling abilities and a large operating temperature range.¹¹

PILs prepared from oxoacids tend to exhibit low overpotentials for H_2 oxidation and O_2 reduction.^{4,26,27} Among the oxoacids, triflic acid (CF_3SO_3H) is a superacid with a pK_a of around -14 .²⁸ Appleby and Baker²⁹ reported that the oxygen reduction reaction at a Pt surface in $1.1 \text{ mol L}^{-1} CF_3SO_3H$ solution showed apparently greater kinetics than that in $85\% H_3PO_4$ solution at 1 atm and ordinary temperature. Furthermore, CF_3SO_3H is resistant to both oxidation and reduction with a high thermal stability and a relatively low viscosity.^{30,31} Therefore, it can be used in various protonation reactions.

The present work compares the physicochemical properties of phosphonium-based and ammonium-based PILs with either electron-donating or electron-withdrawing groups:

^aCentre for Surface Chemistry and Catalysis, Faculty of Bioscience Engineering, KU Leuven, Kasteelpark Arenberg 23, Box 2461, Leuven, 3001, Belgium. E-mail: ivo.vankelecom@biw.kuleuven.be; Fax: +32 16 321998; Tel: +32 16 321594

^bNEXT ENERGY · EWE-Forschungszentrum für Energietechnologie e. V., Carl-von-Ossietzky-Str. 15, D-26129 Oldenburg, Germany

^cHySAI/Catalysis, Dept. of Chemical Engineering, University of Cape Town, Private Bag X3, Rondebosch, Cape Town, 7701, South Africa. E-mail: olaf.conrad@uct.ac.za; Tel: +27 21 650 4366

† Electronic supplementary information (ESI) available: Pictures of as-synthesized PILs and the emulsion of $[Oct_3NH][TfO]$ dispersed in water; detailed IR analysis. See DOI: 10.1039/c2jm34359b

trioctylphosphonium triflate ($[\text{Oct}_3\text{PH}][\text{TfO}]$), trioctylammonium triflate ($[\text{Oct}_3\text{NH}][\text{TfO}]$), triphenylphosphonium triflate ($[\text{Ph}_3\text{PH}][\text{TfO}]$) and triphenylammonium triflate ($[\text{Ph}_3\text{NH}][\text{TfO}]$).[‡] The phosphonium-based PILs showed attractive advantages in terms of thermal stability and ionic conductivity over their ammonium analogues as non-aqueous electrolytes.

2. Experimental

2.1 Chemicals

Tri-*n*-octylphosphine ($[\text{CH}_3(\text{CH}_2)_7]_3\text{P}$, 97%, Aldrich), tri-*n*-octylamine ($[\text{CH}_3(\text{CH}_2)_7]_3\text{N}$, 98%, Acros Organics), triphenylphosphine ($(\text{C}_6\text{H}_5)_3\text{P}$, 99%, Alfa Aesar), triphenylamine ($(\text{C}_6\text{H}_5)_3\text{N}$, $\geq 99.0\%$, Acros Organics) and $\text{CF}_3\text{SO}_3\text{H}$ (98%, Sigma-Aldrich) were used as received. $[\text{Oct}_3\text{PH}][\text{TfO}]$, $[\text{Oct}_3\text{NH}][\text{TfO}]$, $[\text{Ph}_3\text{PH}][\text{TfO}]$ and $[\text{Ph}_3\text{NH}][\text{TfO}]$ were prepared in a dry glove box by equimolar combination of the respective Brønsted bases and $\text{CF}_3\text{SO}_3\text{H}$. All the mixtures were heated above the melting point for 5 h to promote the formation of the PILs. All the synthesized PILs were found to be oily and hydrophobic, which should be closely related to the octyl or phenyl groups.[†] The chemical structures are displayed in Fig. 1.

2.2 Thermal analysis

Thermogravimetric analysis (TGA) for each PIL was recorded on a thermogravimetric analyzer (TGA 4000, PerkinElmer) in a stream of N_2 (30 mL min^{-1}) with an open Al_2O_3 pan. The heating rate was 10 K min^{-1} . The temperature corresponding to 10% mass loss during the heating scan was used as the decomposition temperature (T_d). Thermal stability in O_2 was studied by heating each PIL in a stream of O_2 (30 mL min^{-1}) at a heating rate of 10 K min^{-1} using the above apparatus. All the above sample weights were controlled to be between 12 and 15 mg.

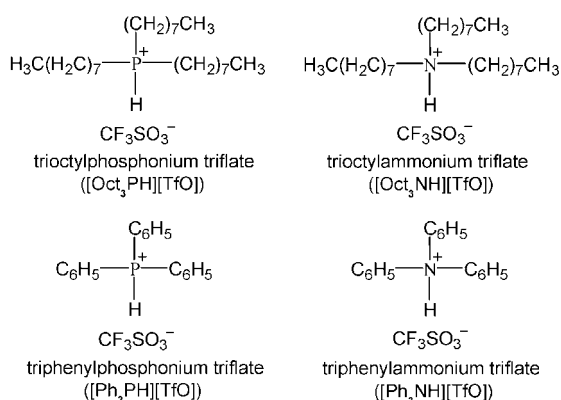


Fig. 1 Chemical structures of $[\text{Oct}_3\text{PH}][\text{TfO}]$, $[\text{Oct}_3\text{NH}][\text{TfO}]$, $[\text{Ph}_3\text{PH}][\text{TfO}]$ and $[\text{Ph}_3\text{NH}][\text{TfO}]$.

[‡] Although the melting points of the protic salts should be lower than 100°C to qualify the liquids as protic ionic liquids (PILs) by the familiar criterion, PILs are used here to refer to all protic molten salts for convenience.

Isothermal chronogravimetric experiments were conducted on the same instrument under N_2 atmosphere (30 mL min^{-1}) at 250°C for $[\text{Oct}_3\text{PH}][\text{TfO}]$ and $[\text{Oct}_3\text{NH}][\text{TfO}]$, respectively. Each sample weight was about 22 g.

Differential scanning calorimetry (DSC) measurements were performed on a Netzsch DSC 204 *FI Phoenix* apparatus under N_2 atmosphere. Samples around 10 mg each were tightly sealed in Al pans. The samples were heated from room temperature to 200°C and then cooled to -150°C and heated again to 200°C at cooling and heating rates of 10 K min^{-1} . Glass transition temperature (T_g , onset temperature of the heat capacity change) and melting temperature (T_m , onset temperature of the corresponding endothermic peak) were determined from the DSC thermograms recorded during the reheating scans.

2.3 Fourier transform infrared (FT-IR) spectra

Fourier transform infrared (FT-IR) spectra were recorded at room temperature on a PerkinElmer Spectrum 100 FT-IR spectrometer with universal ATR accessory at a spectral resolution of 4 cm^{-1} .

2.4 Ionic conductivity

The ionic conductivities of each PIL were measured above the respective melting points from low temperature to high temperature by complex impedance spectroscopy. The temperature was controlled at 10 K interval ($\pm 0.01 \text{ K}$). The experimental details have been described previously.⁹

2.5 Ion volume calculation

The cation volume (V_{cation}) and anion volume (V_{anion}) for each PIL were computed at the B3LYP/aug-cc-pVDZ//B3LYP/cc-pVDZ level of theory with Gaussian 09 package (Gaussian, Inc.).³²

3. Results and discussion

3.1 Thermal analysis

Fig. 2a shows the TG curves of each PIL in N_2 at a heating rate of 10 K min^{-1} . The TG curves of $[\text{Oct}_3\text{PH}][\text{TfO}]$ and $[\text{Oct}_3\text{NH}][\text{TfO}]$ both exhibit a one-step weight loss process. The values of T_d are listed in Table 1. Obviously, while the T_d of $[\text{Oct}_3\text{PH}][\text{TfO}]$ is only slightly higher than that of $[\text{Oct}_3\text{NH}][\text{TfO}]$, $[\text{Ph}_3\text{PH}][\text{TfO}]$ has a much higher T_d than $[\text{Ph}_3\text{NH}][\text{TfO}]$. In particular, the TG curve of $[\text{Ph}_3\text{NH}][\text{TfO}]$ even shows an initial weight loss event from the starting temperature of 30°C . This should be attributed to the weight loss of free $\text{CF}_3\text{SO}_3\text{H}$ as revealed by FT-IR analysis below. Furthermore, Ph_3N has an estimated $\text{p}K_a < 0$ and rarely forms salts.³³ (Nevertheless, triphenylammonium fluoroborate, a pale green oil, has been reported in the literature.³⁴) In the solid state, the Ph_3N molecule is almost planar at the central N atom, allowing for maximum orbital overlap with the π -system.^{34–36} In contrast, the Ph_3P molecule has a pyramidal configuration around the P atom in the solid state and has a weaker p π conjugation between the lone electron pair of the central P atom and π electrons of the adjoining phenyl group and thus should have much more basic character.^{35,37} Therefore, the driving force

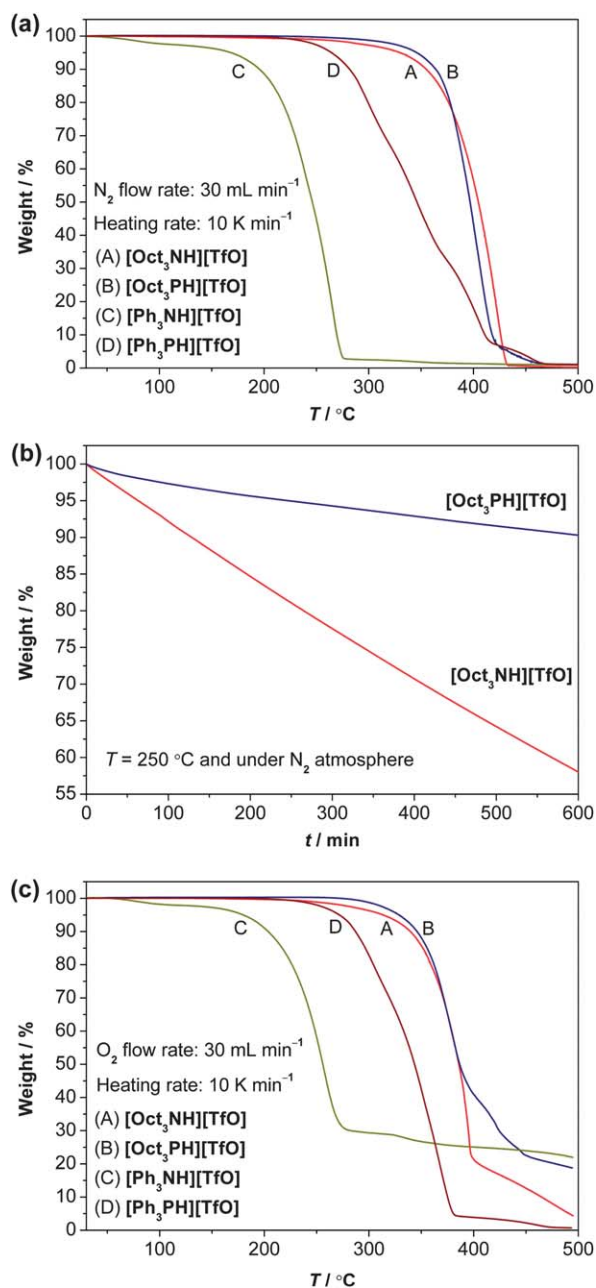


Fig. 2 (a) TG curves in N₂ (10 K min⁻¹), (b) isothermal chronogravimetric plots for [Oct₃PH][TfO] and [Oct₃NH][TfO] at 250 °C, and (c) TG curves in O₂ (10 K min⁻¹).

Table 1 Thermal properties of each PIL

PIL	T_g^a /K	T_m^b /°C	T_d^c /°C
[Oct ₃ NH][TfO]	186	9	363
[Oct ₃ PH][TfO]	185	51	371
[Ph ₃ NH][TfO]	261	117	208
[Ph ₃ PH][TfO]	277	125 ^d	292

^a Onset temperature of the heat capacity change for glass transition (T_g).

^b Onset temperature of the corresponding endothermic peak (T_m).

^c Temperature of 10% mass loss in the TGA experiment (T_d). ^d The observed T_m of [Ph₃PH][TfO] during slow heating was slightly lower than 120 °C.

for proton transfer from CF₃SO₃H to Ph₃N is relatively weaker, resulting in a “poor” ionic liquid.³⁸ This has also been indicated by the much lower thermal stability of [Ph₃NH][TfO] with a T_d of 208 °C. Watanabe *et al.*³⁹ have reported a similar Brønsted acid–base complex, which was prepared from the combination of 2,5-diphenyl-1,3,4-oxadiazole (DOD) and bis-(trifluoromethanesulfonyl)imide (HTFSI), which is also a superacid. The poor thermal stability of the [DOD]/[HTFSI] = 5/5 complex was due to the elimination of free HTFSI from it.³⁹

The isothermal weight loss curves depicted in Fig. 2b further reveal the superior thermal stability of [Oct₃PH][TfO] compared with [Oct₃NH][TfO], indicating that phosphonium-based PILs are thermally more stable than their ammonium analogues, no matter whether the P and N center atoms are bonded to electron-donating octyl or electron-withdrawing phenyl. Furthermore, Fig. 2c demonstrates that these PILs all have good thermal stability in O₂ except [Ph₃NH][TfO].

The electron-withdrawing phenyl seems to weaken the thermal stability of both phosphonium and ammonium based PILs compared with electron-donating octyl. This might be attributed to the induced lower electron density of P and N atoms by phenyl, leading to lower basicity of the Brønsted bases and hence weaker thermal stability of the PILs. It has been shown that PILs prepared from stronger Brønsted bases tend to have higher thermal stability.^{28,40}

3.2 FT-IR analysis

The observed FT-IR spectra demonstrate the formation of the proton transfer salts. As shown in Fig. 3a, the absence of O–H stretching bands between 3400 and 3800 cm⁻¹ confirms qualitatively the very low water contents of the PILs.

For ammonium-based PILs, the region of 3200–2400 cm⁻¹ is characteristic of ammonium structures.^{9,41–43} For example, the bands at 3042 and 2812 cm⁻¹ are attributed to the N–H stretching vibration for [Oct₃NH][TfO].⁴³ For [Ph₃NH][TfO], the N–H frequencies are split and appear at 2926, 2843, 2735 and 2555 cm⁻¹, whose position and appearance provide spectroscopic evidence for the presence of hydrogen bonding between cation and anion in the salt.³⁴ According to Reed *et al.*,⁴³ for trialkylammonium salts with weakly basic anions A⁻ such as CF₃SO₃⁻, weaker NH⋯A⁻ hydrogen bond strength means higher N–H stretching frequencies. Compared with the split broad N–H stretching bands of [Ph₃NH][TfO], the higher N–H stretching frequencies of [Oct₃NH][TfO] confirm that Oct₃N is more basic than Ph₃N and indicate that the NH⋯A⁻ hydrogen bonds inside [Oct₃NH][TfO] may be relatively weaker than those inside [Ph₃NH][TfO].

For [Oct₃PH][TfO], the P–H stretching bands may be overlapped with C–H vibrational bands in the region of 3000–2800 cm⁻¹ when the frequency is lower than 3000 cm⁻¹,[†] resembling the case of the N–H stretching frequencies.⁴³ For [Ph₃PH][TfO], compared with the IR spectra of CF₃SO₃H and Ph₃P,^{44–46} a new, broad and medium strong peak appearing at 2405 cm⁻¹ is very likely due to the P–H stretching vibration.

As displayed in Fig. 3b, the formation of CF₃SO₃⁻ anions in each PIL is confirmed by the following bands: 1289, 1235, 1222, 1159, 1027 and 757 cm⁻¹ for [Oct₃NH][TfO]; 1255, 1223, 1155, 1031 and 755 cm⁻¹ for [Oct₃PH][TfO]; 1275, 1230, 1155 and 1023

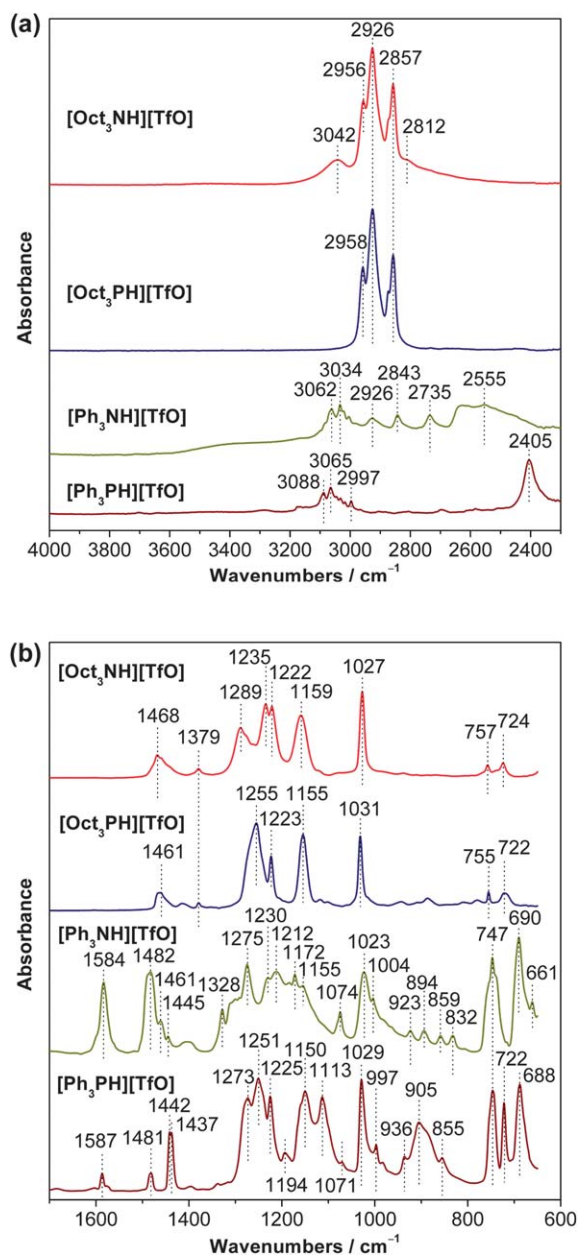


Fig. 3 FT-IR spectra of the PILs at room temperature in the region of (a) 2200–4000 cm^{-1} and (b) 650–1700 cm^{-1} .

cm^{-1} for $[\text{Ph}_3\text{NH}][\text{TfO}]$; 1273, 1251, 1225, 1150 and 1029 cm^{-1} for $[\text{Ph}_3\text{PH}][\text{TfO}]$.^{47,48} In addition, the octyl functional groups in $[\text{Oct}_3\text{NH}][\text{TfO}]$ and $[\text{Oct}_3\text{PH}][\text{TfO}]$ are evidenced by the peaks at 2956, 2926, 2857, 1468, 1379, 724 cm^{-1} and 2958, 2926, 2857, 1461, 1379, 722 cm^{-1} , respectively.⁴⁹ The mono-substituted benzene rings of $[\text{Ph}_3\text{NH}][\text{TfO}]$ and $[\text{Ph}_3\text{PH}][\text{TfO}]$ are marked by the bands at 3062, 3034, 1584, 1482, 1461, 1445, 747, 690 cm^{-1} and 3088, 3065, 2997, 1587, 1481, 1442, 1437, 747, 688 cm^{-1} , respectively.^{50,51} The detailed analysis of these bands is given in the ESI.†

Particularly, for $[\text{Ph}_3\text{NH}][\text{TfO}]$, while the sharp bands at 1328, 1172 and 894 cm^{-1} indicate the existence of some Ph_3N in $[\text{Ph}_3\text{NH}][\text{TfO}]$ (*i.e.* the equimolar combination of Ph_3NH and $\text{CF}_3\text{SO}_3\text{H}$),³⁴ a certain amount of $\text{CF}_3\text{SO}_3\text{H}$ seems to also persist

in it as revealed by the peak at 1212 and 923 cm^{-1} associated with free $\text{CF}_3\text{SO}_3\text{H}$.^{44,52,53} This again showed the relatively weak complex between Ph_3NH and $\text{CF}_3\text{SO}_3\text{H}$.

In addition to inter-ionic interactions such as Coulombic interactions and van der Waals forces seen in aprotic ionic liquids, Watanabe *et al.*⁵⁴ have experimentally established that strong hydrogen bonds between the protonated cation and anion are present in PILs through N–H bonds. The broadening of N–H stretching vibration peaks of $[\text{Oct}_3\text{NH}][\text{TfO}]$ (*e.g.* at 3042 and 2812 cm^{-1}) and $[\text{Ph}_3\text{NH}][\text{TfO}]$ (*e.g.* at 2555 cm^{-1}) in the range of 3200–2400 cm^{-1} indicates that the ammonium-based PILs exist in a strongly hydrogen-bonded network.^{9,34,41,42,55} However, for $[\text{Oct}_3\text{PH}][\text{TfO}]$, no obvious broadening is observed, suggesting weaker hydrogen bonds inside it.

On the one hand, the covalent radius of P (110.7 pm) is reported to be larger than that of N (73.4 pm).⁵⁶ Table 2 further shows that $[\text{Oct}_3\text{PH}][\text{TfO}]$ and $[\text{Ph}_3\text{PH}][\text{TfO}]$ have larger calculated V_{cation} than $[\text{Oct}_3\text{NH}][\text{TfO}]$ and $[\text{Ph}_3\text{NH}][\text{TfO}]$, respectively, indicating weaker Coulombic interactions between cations and anions inside the corresponding phosphonium-based PILs. Matsumiya *et al.* have shown that the Coulombic interaction between the cation and the anion in phosphonium-based AILs is weaker than that in ammonium counterparts.¹⁷ It should be noted that in their reported AILs the inter-ionic interactions are mainly Coulombic interactions and van der Waals forces. Furthermore, the lattice potential energy (U_{POT}) of these PILs may be estimated using the following empirical equation:⁵⁷

$$U_{\text{POT}}/\text{kJ mol}^{-1} = 2 \left(\frac{117.3}{V_{\text{m}}^{1/3}} + 51.9 \right) \quad (1)$$

where V_{m} is the molecular volume in units of nm^3 ($V_{\text{m}} = V_{\text{cation}} + V_{\text{anion}}$) and $U_{\text{POT}} < 5000 \text{ kJ mol}^{-1}$. As shown in Table 2, the calculated values of U_{POT} of phosphonium-based PILs are lower than those of their ammonium analogues, suggesting weaker Coulombic interactions inside the former. As the Coulombic interactions between the cation and the anion of the PIL tend to cause a decrease in mobility,¹ phosphonium-based PILs are expected to have higher ionic conductivities than their ammonium counterparts.

On the other hand, as discussed above, the Coulombic interactions inside $[\text{Oct}_3\text{PH}][\text{TfO}]$ should be weaker than those inside $[\text{Oct}_3\text{NH}][\text{TfO}]$ and hence a lower T_{m} for the former would be expected. However, as shown in Table 1, T_{m} of $[\text{Oct}_3\text{PH}][\text{TfO}]$ is about 42 K higher than T_{m} of $[\text{Oct}_3\text{NH}][\text{TfO}]$. Since the molecular structures of $[\text{Oct}_3\text{PH}][\text{TfO}]$ and $[\text{Oct}_3\text{NH}][\text{TfO}]$ are highly similar and the molecular weight of $[\text{Oct}_3\text{PH}][\text{TfO}]$ is only slightly higher, the relatively weak van der Waals forces should

Table 2 Cation volume (V_{cation}), molecular volume (V_{m}) and lattice potential energy (U_{POT}) of each PIL

PIL	$V_{\text{cation}}^a/\text{nm}^3$	$V_{\text{m}}^b/\text{nm}^3$	$U_{\text{POT}}/\text{kJ mol}^{-1}$
$[\text{Oct}_3\text{NH}][\text{TfO}]$	0.512	0.632	377
$[\text{Oct}_3\text{PH}][\text{TfO}]$	0.618	0.738	363
$[\text{Ph}_3\text{NH}][\text{TfO}]$	0.311	0.431	414
$[\text{Ph}_3\text{PH}][\text{TfO}]$	0.346	0.466	406

^a The calculated triflate anion volume is 0.120 nm^3 . ^b $V_{\text{m}} = V_{\text{cation}} + V_{\text{anion}}$.

Table 3 VFT fitting parameters for the ionic conductivity

PIL	$A/S\text{ K}^{1/2}\text{ cm}^{-1}$	B/K	T_0/K	R^{2a}
[Oct ₃ NH][TfO]	5.018 ± 0.306	1340 ± 26	151.8 ± 2.0	0.9999
[Oct ₃ PH][TfO]	9.752 ± 0.447	1231 ± 20	173.5 ± 1.8	0.9999
[Ph ₃ NH][TfO]	3.453 ± 0.499	758.5 ± 53.4	242.4 ± 6.4	0.9999
[Ph ₃ PH][TfO]	11.43 ± 0.316	717.3 ± 10.6	235.2 ± 1.4	0.9999

^a R^2 : correlation coefficient.

be comparable. Therefore, the obvious difference in T_m should be attributed to the strength of hydrogen bonding. Opposite to the behavior of hydrogen bonds in liquids and solutions consisting purely of neutral molecules, Ludwig *et al.*^{58,59} reported that strong hydrogen bonds formed between cations and anions introduce “defects” into the Coulomb network of ILs and increase the dynamics of the cations and anions, resulting in decreased melting points. Similarly, the stronger hydrogen bond interactions inside [Oct₃NH][TfO] may fluidize the PIL and lead to a remarkably lower T_m than that of [Oct₃PH][TfO].

3.3 Ion conduction behavior

Fig. 4a confirms that phosphonium-based PILs have higher ionic conductivity than the corresponding ammonium-based PILs.

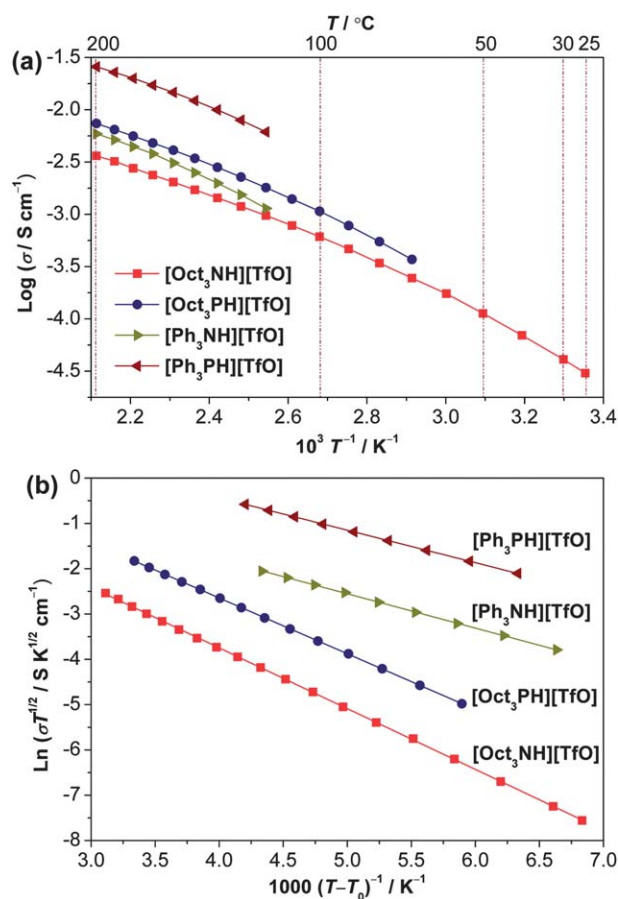


Fig. 4 (a) Arrhenius plots and (b) VFT plots for the ionic conductivity of phosphonium-based and ammonium-based protic ionic liquids.

Particularly, [Oct₃NH][TfO] is a room temperature ionic liquid with an ionic conductivity of $3.03 \times 10^{-5}\text{ S cm}^{-1}$ at 25 °C. As the temperature dependence of ionic conductivity exhibits deviation from a simple Arrhenius behavior, the Vogel–Fulcher–Tamman (VFT) equation is used to describe the ion conduction behavior:⁶⁰

$$\sigma(T) = \frac{A}{\sqrt{T}} \exp\left(\frac{-B}{T - T_0}\right) \quad (2)$$

where A is proportional to the concentration of carrier ions, B is the pseudoactivation energy for ion conduction, and T_0 is the ideal glass transition temperature.⁶¹ A , B and T_0 were all adjustable parameters. The best-fit parameters are listed in Table 3. The VFT plots are demonstrated to be straight lines in Fig. 4b. Clearly, the ion conduction behavior of the as-studied PILs obeys the VFT equation very well. The difference between T_g obtained from DSC measurements and T_0 calculated from the VFT equation (namely $T_g - T_0$) lies in a reasonable range of 10–50 K.⁶¹ [Oct₃PH][TfO] and [Ph₃PH][TfO] are found to have much higher values of A than [Oct₃NH][TfO] and [Ph₃NH][TfO], respectively. This may also explain the higher ionic conductivity of phosphonium-based PILs. As Table 2 shows that phosphonium-based PILs have a comparable V_m with their ammonium counterparts, higher concentrations of carrier ions (effective ionic concentrations) for phosphonium-based PILs may indicate their higher ionicity.^{62–64} Actually, it is reported that tributyl phosphonium PILs exhibit higher degree of ionicity compared with their ammonium analogues.²¹ One reason for why phosphonium-based PILs exhibit higher ionic conductivity than their ammonium analogues might be as follows: the stronger hydrogen bond interactions in the ammonium-based PILs herein may lead to associative diffusion in which the ion pair likely diffuses together as a noncharged species and does not contribute to the direct current ionic conduction,⁶⁵ while weaker hydrogen bond interactions in the corresponding phosphonium-based PILs make the individual ions diffuse more freely, thus resulting in higher ionic conductivity for phosphonium-based PILs. This consideration is supported by higher concentrations of carrier ions of phosphonium-based PILs shown in Table 3.

4. Conclusions

Trioctylphosphonium triflate, trioctylammonium triflate, triphenylphosphonium triflate and triphenylammonium triflate were compared with respect to their physicochemical properties. Phosphonium-based PILs exhibited higher thermal stability and ionic conductivity than their ammonium analogues, no matter whether the P and N center atoms are bonded to the electron-donating octyl groups or the electron-withdrawing phenyl groups. The temperature dependence of the ionic conductivity of the PILs obeys the Vogel–Fulcher–Tamman (VFT) equation very well. The higher ionic conductivity of phosphonium-based PILs may be due to their weaker hydrogen bond and Coulombic interactions as well as higher carrier ion concentrations. In addition, compared with the electron-withdrawing phenyl group, the electron-donating octyl group is advantageous for the thermal stability of both phosphonium-based and ammonium-based PILs. The phosphonium-based PILs are expected to be promising non-aqueous electrolytes for electrochemical applications.

Acknowledgements

J.L. and I.F.J.V. acknowledge IOF-KP 10/005 of KU Leuven for financial support. J.L. deeply thanks Prof. Dr Carsten Agert and Dr Alexander Dyck (NEXT ENERGY) for their financial support and the opportunity to conduct the experimental work at NEXT ENERGY. We appreciate Prof. Dr Tianying Yan (Nankai University) for the help of ion volume calculation. We are grateful to Prof. Dr Koen Binnemans (KU Leuven) for technical discussions.

Notes and references

- 1 T. L. Greaves and C. J. Drummond, *Chem. Rev.*, 2008, **108**, 206.
- 2 M. Armand, F. Endres, D. R. MacFarlane, H. Ohno and B. Scrosati, *Nat. Mater.*, 2009, **8**, 621.
- 3 W. Xu and C. A. Angell, *Science*, 2003, **302**, 422.
- 4 H. Nakamoto and M. Watanabe, *Chem. Commun.*, 2007, 2539.
- 5 T. Mizumo, T. Watanabe and H. Ohno, *Polym. J.*, 2008, **40**, 1099.
- 6 F. Yan, S. Yu, X. Zhang, L. Qiu, F. Chu, J. You and J. Lu, *Chem. Mater.*, 2009, **21**, 1480.
- 7 Y. S. Ye, M. Y. Cheng, J. Y. Tseng, G.-W. Liang, J. Rick, Y. J. Huang, F. C. Chang and B. J. Hwang, *J. Mater. Chem.*, 2011, **21**, 2723.
- 8 L. Wang, S. G. Advani and A. K. Prasad, *Electrochem. Solid-State Lett.*, 2012, **15**, B44.
- 9 J. Luo, J. Hu, W. Saak, R. Beckhaus, G. Wittstock, I. F. J. Vankelecom, C. Agert and O. Conrad, *J. Mater. Chem.*, 2011, **21**, 10426.
- 10 L. Timperman, P. Skowron, A. Boisset, H. Galiano, D. Lemordant, E. Frackowiak, F. Béguin and M. Anouti, *Phys. Chem. Chem. Phys.*, 2012, **14**, 8199.
- 11 L. Timperman, H. Galiano, D. Lemordant and M. Anouti, *Electrochem. Commun.*, 2011, **13**, 1112.
- 12 B. Nuthakki, T. L. Greaves, I. Krodziewska, A. Weerawardena, M. I. Burgar, R. J. Mulder and C. J. Drummond, *Aust. J. Chem.*, 2007, **60**, 21.
- 13 K. Fumino, A. Wulf and R. Ludwig, *Angew. Chem., Int. Ed.*, 2009, **48**, 3184.
- 14 K. J. Fraser and D. R. MacFarlane, *Aust. J. Chem.*, 2009, **62**, 309.
- 15 C. J. Bradaric, A. Downard, C. Kennedy, A. J. Robertson and Y. Zhou, *Green Chem.*, 2003, **5**, 143.
- 16 K. Tsunashima and M. Sugiya, *Electrochem. Commun.*, 2007, **9**, 2353.
- 17 M. Matsumiya, S. Suda, K. Tsunashima, M. Sugiya, S. Kishioka and H. Matsuura, *J. Electroanal. Chem.*, 2008, **622**, 129.
- 18 K. Tsunashima, S. Kodama, M. Sugiya and Y. Kunugi, *Electrochim. Acta*, 2010, **56**, 762.
- 19 S. Seki, K. Hayamizu, S. Tsuzuki, K. Fujii, Y. Umebayashi, T. Mitsugi, T. Kobayashi, Y. Ohno, Y. Kobayashi, Y. Mita, H. Miyashiro and S. Ishiguro, *Phys. Chem. Chem. Phys.*, 2009, **11**, 3509.
- 20 N. W. Duffy and A. M. Bond, *Electrochem. Commun.*, 2006, **8**, 892.
- 21 U. A. Rana, R. Vijayaraghavan, M. Walther, J. Sun, A. A. J. Torriero, M. Forsyth and D. R. MacFarlane, *Chem. Commun.*, 2011, **47**, 11612.
- 22 L. Timperman and M. Anouti, *Ind. Eng. Chem. Res.*, 2012, **51**, 3170.
- 23 M. Picquet, S. Stutzmann, I. Tkatchenko, I. Tommasi, J. Zimmermann and P. Wasserscheid, *Green Chem.*, 2003, **5**, 153.
- 24 B. Mariampillai, J. Alliot, M. Li and M. Lautens, *J. Am. Chem. Soc.*, 2007, **129**, 15372.
- 25 P. Thansandote, D. G. Hulcoop, M. Langer and M. Lautens, *J. Org. Chem.*, 2009, **74**, 1673.
- 26 J. Thomson, P. Dunn, L. Holmes, J.-P. Belieres, C. A. Angell and D. Gervasio, *ECS Trans.*, 2008, **13**, 21.
- 27 T. Yasuda, A. Ogawa, M. Kanno, K. Mori, K. Sakakibara and M. Watanabe, *Chem. Lett.*, 2009, **38**, 692.
- 28 J.-P. Belieres and C. A. Angell, *J. Phys. Chem. B*, 2007, **111**, 4926.
- 29 A. J. Appleby and B. S. Baker, *J. Electrochem. Soc.*, 1978, **125**, 404.
- 30 R. D. Howells and J. D. Mc Cown, *Chem. Rev.*, 1977, **77**, 69.
- 31 P. J. Stang and M. R. White, *Aldrichimica Acta*, 1983, **16**, 15.
- 32 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, *Gaussian 09, Revision A.2*, Gaussian, Inc., Wallingford, CT, 2009.
- 33 T. Manifar and S. Rohani, *Can. J. Chem. Eng.*, 2004, **82**, 323.
- 34 R. D. W. Kemmitt, R. H. Nuttall and D. W. A. Sharp, *J. Chem. Soc.*, 1960, 46.
- 35 A. N. Sobolev, V. K. Belsky, I. P. Romm, N. Y. Chernikova and E. N. Guryanova, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1985, **41**, 967.
- 36 X. Wu, A. P. Davis, P. C. Lambert, L. K. Steffen, O. Toy and A. J. Fry, *Tetrahedron*, 2009, **65**, 2408.
- 37 J. J. Daly, *J. Chem. Soc.*, 1964, 3799.
- 38 M. Yoshizawa, W. Xu and C. A. Angell, *J. Am. Chem. Soc.*, 2003, **125**, 15411.
- 39 H. Matsuoka, H. Nakamoto, M. A. B. H. Susan and M. Watanabe, *Electrochim. Acta*, 2005, **50**, 4015.
- 40 H. Luo, G. A. Baker, J. S. Lee, R. M. Pagni and S. Dai, *J. Phys. Chem. B*, 2009, **113**, 4181.
- 41 K. Mori, S. Hashimoto, T. Yuzuri and K. Sakakibara, *Bull. Chem. Soc. Jpn.*, 2010, **83**, 328.
- 42 V. H. Alvarez, S. Mattedi, M. Martin-Pastor, M. Aznar and M. Iglesias, *Fluid Phase Equilib.*, 2010, **299**, 42.
- 43 E. S. Stoyanov, K.-C. Kim and C. A. Reed, *J. Am. Chem. Soc.*, 2006, **128**, 8500.
- 44 P. Laffamme, A. Beaudoin, T. Chapaton, C. Spino and A. Soldera, *J. Comput. Chem.*, 2012, **33**, 1190.
- 45 S. P. Gejji, K. Hermansson and J. Lindgren, *J. Phys. Chem.*, 1993, **97**, 6986.
- 46 R. J. H. Clark, C. D. Flint and A. J. Hempleman, *Spectrochim. Acta, Part A*, 1987, **43**, 805.
- 47 C. M. Burba, N. M. Rocher, R. Frech and D. R. Powell, *J. Phys. Chem. B*, 2008, **112**, 2991.
- 48 A. Bernson and J. Lindgren, *Solid State Ionics*, 1993, **60**, 37.
- 49 W. Abdallah and U. Yilmazer, *Thermochim. Acta*, 2011, **525**, 129.
- 50 J. Tang, X. Jing, B. Wang and F. Wang, *Synth. Met.*, 1988, **24**, 231.
- 51 D. L. Ou and A. B. Seddon, *J. Non-Cryst. Solids*, 1997, **210**, 187.
- 52 C. M. Burba, N. M. Rocher and R. Frech, *J. Phys. Chem. B*, 2009, **113**, 11453.
- 53 Y. Katsuhara, R. M. Hammaker and D. D. DesMarteau, *Inorg. Chem.*, 1980, **19**, 607.
- 54 M. S. Miran, H. Kinoshita, T. Yasuda, M. A. B. H. Susan and M. Watanabe, *Chem. Commun.*, 2011, **47**, 12676.
- 55 J. Luo, T. V. Tan, O. Conrad and I. F. J. Vankelecom, *Phys. Chem. Chem. Phys.*, 2012, **14**, 11441.
- 56 R. T. Sanderson, *J. Am. Chem. Soc.*, 1983, **105**, 2259.
- 57 H. D. B. Jenkins, D. Tudela and L. Glasser, *Inorg. Chem.*, 2002, **41**, 2364.
- 58 K. Fumino, A. Wulf and R. Ludwig, *Angew. Chem., Int. Ed.*, 2008, **47**, 8731.
- 59 K. Fumino, T. Peppel, M. Geppert-Rybczyńska, D. H. Zaitsau, J. K. Lehmann, S. P. Verevkin, M. Köckerling and R. Ludwig, *Phys. Chem. Chem. Phys.*, 2011, **13**, 14064.
- 60 C. A. Angell, *J. Phys. Chem.*, 1964, **68**, 1917.
- 61 S. Seki, M. A. B. H. Susan, T. Kaneko, H. Tokuda, A. Noda and M. Watanabe, *J. Phys. Chem. B*, 2005, **109**, 3886.
- 62 H. Tokuda, S. Tsuzuki, M. A. B. H. Susan, K. Hayamizu and M. Watanabe, *J. Phys. Chem. B*, 2006, **110**, 19593.
- 63 K. Ueno, H. Tokuda and M. Watanabe, *Phys. Chem. Chem. Phys.*, 2010, **12**, 1649.
- 64 D. R. MacFarlane, M. Forsyth, E. I. Izgorodina, A. P. Abbott, G. Annat and K. Fraser, *Phys. Chem. Chem. Phys.*, 2009, **11**, 4962.
- 65 H. Tokuda, K. Ishii, M. A. B. H. Susan, S. Tsuzuki, K. Hayamizu and M. Watanabe, *J. Phys. Chem. B*, 2006, **110**, 2833.