

# In the footsteps of August Michaelis: Syntheses and Thermodynamics of Extremely Low-Volatile Ionic Liquids

Dzmitry H. Zaitsau,<sup>[a]</sup> Anke Topp,<sup>[b]</sup> Antje Siegesmund,<sup>[b]</sup> Ayla Pöpcke,<sup>[b]</sup> Martin Köckerling,<sup>\*,[b]</sup> and Sergey P. Verevkin<sup>\*,[a, c]</sup>

A series of nine different known ionic liquids or low melting salts was synthesised and purified. They are composed of the [NTf<sub>2</sub>]<sup>-</sup> (bis(trifluoromethane)sulfonimide), [OTf]<sup>-</sup> (trifluoromethane-sulfonate), or [B(CN)<sub>4</sub>]<sup>-</sup> (tetracyanidoborate) anion and [Ph<sub>4</sub>P]<sup>+</sup> (tetraphenylphosphonium), [Ph<sub>3</sub>BzP]<sup>+</sup> (triphenylbenzyl phosphonium), [t<sup>n</sup>Bu<sub>4</sub>P]<sup>+</sup> (tetra-<sup>n</sup>butylphosphonium), [t<sup>n</sup>BuPh<sub>3</sub>P]<sup>+</sup> (tri-phenyl-<sup>n</sup>butylphosphonium), [t<sup>n</sup>Bu<sub>4</sub>N]<sup>+</sup> (tetra-<sup>n</sup>butylammonium), or the [PPN]<sup>+</sup> (bis(triphenylphosphine)-iminium) cation. Precise vapour pressure data and enthalpies of

vaporisation were measured using the Quartz Crystal Microbalance (QCM) method and evaluated. Structure-property relations are established using the obtained data as well as literature known data of ILs with alkyl-substituted imidazolium cations. It turns out that ILs with the tetracyanidoborate anion have even higher values of the enthalpy of vaporisation than those with the common [NTf<sub>2</sub>]<sup>-</sup> or [OTf]<sup>-</sup> anion and therefore are even less volatile.

## 1. Introduction

Within about the last two decades a huge number of scientific investigations have been focused on low melting salts, the ionic liquids.<sup>[1]</sup> Doubtless, the fascination of this class of compounds is fuelled up by their interesting properties, such as low vapour pressure, high thermal stability, easily tuneable acidity, high electrochemical stability, high conductivity, high solubility, and more. Because of these unique properties they are promising candidates for useful industrial applications.<sup>[1e,2]</sup> Even though the intensive investigations started around the year 2000, some investigations were reported much earlier. Paul Walden reported for the first time about a room temperature ionic liquid

already in 1914.<sup>[3]</sup> Someone else in this period of time needs to be mentioned also, that is August Michaelis, who was Professor at the University of Rostock from 1890 until 1916 (see for example ref.<sup>[4]</sup>). His research was focused on nitrogen and phosphorus compounds and included phosphonium salts, which are nowadays the cations in many known ionic liquids.<sup>[5]</sup> In this paper we follow the footsteps of August Michaelis and report about properties of nine ionic liquids (or at least salts with low melting points), of which seven contain phosphonium cations, one an iminium, and one an ammonium cation. The Lewis formulas of the investigated compounds are shown in Figure 1.

We report the precise absolute vapour pressures and enthalpies of vaporisation,  $\Delta^g H_m^o$ , of these ionic liquids, which were measured using the quartz-crystal microbalance (QCM) method. These experimental results were used to understand

[a] Dr. D. H. Zaitsau, Prof. Dr. S. P. Verevkin  
Department of Physical Chemistry and Faculty of Interdisciplinary Research Competence Centre CALOR  
University of Rostock  
Dr.-Lorenz-Weg 2  
18059 Rostock (Germany)  
E-mail: sergey.verevkin@uni-rostock.de

[b] Dr. A. Topp, Dr. A. Siegesmund, A. Pöpcke, Prof. Dr. M. Köckerling  
Department of Inorganic Chemistry  
Solid State Chemistry Group and Faculty of Interdisciplinary Research  
University of Rostock  
Albert-Einstein-Str. 3a  
18059 Rostock (Germany)  
E-mail: Martin.Koeckerling@uni-rostock.de

[c] Prof. Dr. S. P. Verevkin  
Department of Physical Chemistry  
Kazan Federal University  
Kremlevskaya Str. 18  
420008 Kazan (Russia)

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An invited contribution to a Special Issue dedicated to Material Synthesis in Ionic Liquids

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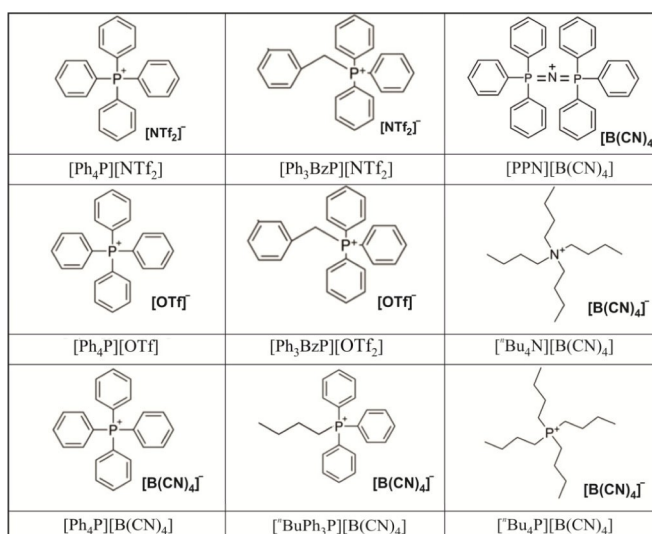


Figure 1. Structures of the molten salts studied in this work.

structure-property relationships in these extremely heavy volatile ionic liquids.

## 2. Results and Discussion

### 2.1. Melting Temperatures

The melting (fusion) temperatures of the ionic liquids under investigation were published by our group before or determined using the DSC (differential scanning calorimetry) as described in the experimental section.<sup>[5b,6]</sup> The values are listed in Table 1. They fall in the range from 246.2 K to 585.9 K thereby classifying them in RTILs, ILs or low melting salts.

### 2.2. Experimental Vaporisation Enthalpies

All compounds studied in this work with the exception of [<sup>n</sup>BuPh<sub>3</sub>P][B(CN)<sub>4</sub>] are solids at the room temperature (see Table 1). However, except for [Ph<sub>4</sub>P][OTf], the vapour pressures temperature dependences have been studied above melting points and the standard molar enthalpies of vaporisation  $\Delta_i^g H_m^o$  ( $T_{av}$ ) derived for ILs. These results are presented in Table 2. For [Ph<sub>4</sub>P][OTf] vapour pressures were measured in the range below the melting point and from these data the standard molar enthalpy of sublimation  $\Delta_i^g H_m^o$  ( $T_{av}$ ) is derived (see Table 2). As a rule, thermochemical values are commonly referenced to the temperature  $T=298.15$  K in order to compare and to reveal structure-property relationships. Thus, the vaporisation enthalpies were adjusted to the reference temperature,  $\Delta_i^g H_m^o$  (298.15 K), according to the Kirchoff's equation:

$$\Delta_i^g H_m^o (298.15 \text{ K}) = \Delta_i^g H_m^o (T_{av}) + \Delta C_{p,m}^o \times (T_{av} - 298.15 \text{ K}) \quad (1)$$

**Table 1.** Fusion temperatures derived from DSC measurements<sup>[5b,6]</sup>

IL	$T_{fus}/\text{K}$
[Ph <sub>4</sub> P][NTf <sub>2</sub> ]	408.3
[Ph <sub>3</sub> BzP][NTf <sub>2</sub> ]	404.8
[Ph <sub>4</sub> P][OTf]	585.9
[Ph <sub>3</sub> BzP][OTf]	467.1
[ <sup>n</sup> Bu <sub>4</sub> P][B(CN) <sub>4</sub> ]	316.2
[ <sup>n</sup> BuPh <sub>3</sub> P][B(CN) <sub>4</sub> ]	246.2
[Ph <sub>4</sub> P][B(CN) <sub>4</sub> ]	466.2
[PPN][B(CN) <sub>4</sub> ]	435.2
[ <sup>n</sup> Bu <sub>4</sub> N][B(CN) <sub>4</sub> ]	316.2

The value  $\Delta_i^g C_{p,m}^o = C_{p,m}^o(\text{g}) - C_{p,m}^o(\text{liq})$  is the difference between the molar heat capacities of the gaseous  $C_{p,m}^o(\text{g})$  and the liquid phase  $C_{p,m}^o(\text{liq})$ , respectively. Equation (1) is also valid for the temperature adjustment of the sublimation enthalpy,  $\Delta_i^g H_m^o$  ( $T_{av}$ ), of [Ph<sub>4</sub>P][OTf] by using the  $\Delta_i^g C_{p,m}^o$  instead of  $\Delta_i^g C_{p,m}^o$  values. Data required for temperature adjustments of vaporisation/sublimation enthalpies are developed in this work and given in the electronic Supporting information.

The final experimental vaporisation enthalpies at  $T=298.15$  K,  $\Delta_i^g H_m^o$  (298.15 K), are listed in Table 2, and are discussed in the following section with respect to structure-property relationships.

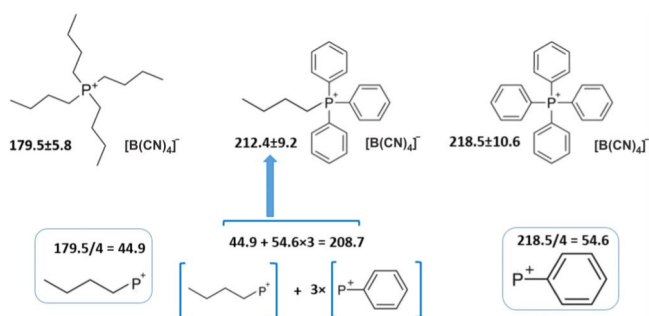
### 2.3. Vaporisation Enthalpies of Ionic Liquids: Structure-Property Relationships

Carefully measured vaporisation enthalpies  $\Delta_i^g H_m^o$  (298.15 K) are compiled in Table 2. They have been measured for the first time. The question arises if these values are reliable? Are these new values consistent with available knowledge on vaporisation thermodynamics of ionic liquids? The only way to answer these questions is to do a structure-property analysis as follows.

**Table 2.** Thermodynamics of vaporisation/sublimation derived from QCM measurement.

	T-range [K]	$T_{av}$ [K]	$C_{p,m}^o$ [a] [J·K <sup>-1</sup> ·mol <sup>-1</sup> ]	$-\Delta_i^g C_{p,m}^o$ [kJ·mol <sup>-1</sup> ]	$\Delta_i^g C_{p,m}^o$ ( $T_{av}$ ) <sup>[b]</sup> [kJ·mol <sup>-1</sup> ]	$\Delta_i^g H_m^o$ ( $T_{av}$ ) [kJ·mol <sup>-1</sup> ]	$\Delta_i^g H_m^o$ (298.15 K) <sup>[c]</sup> [kJ·mol <sup>-1</sup> ]
[Ph <sub>4</sub> P][NTf <sub>2</sub> ]	473–426	449.4	763 <sup>[a]</sup>	130 <sup>[d]</sup>	87.4 ± 1.6	160.5 ± 1.2	180.2 ± 4.1
[Ph <sub>3</sub> BzP][NTf <sub>2</sub> ]	468–421	444.5	795 <sup>[a]</sup>	138 <sup>[d]</sup>	86.7 ± 1.6	158.9 ± 1.0	179.1 ± 4.2
[Ph <sub>4</sub> P][OTf] (cr)	527–501	512.4	897 <sup>[e]</sup>	32 <sup>[f]</sup>	118.8 ± 1.6	216.2 ± 2.6	229.7 ± 3.7 <sup>[g]</sup>
[Ph <sub>3</sub> BzP][OTf]	494–446	469.8	929 <sup>[e]</sup>	107 <sup>[f]</sup>	87.5 ± 1.6	168.7 ± 1.0	202.3 ± 8.4 <sup>[h]</sup>
[ <sup>n</sup> Bu <sub>4</sub> P][B(CN) <sub>4</sub> ]	390–437	412.7	701 <sup>[e]</sup>	251 <sup>[d]</sup>	82.2 ± 1.6	150.7 ± 1.0	187.1 ± 3.8
[ <sup>n</sup> BuPh <sub>3</sub> P][B(CN) <sub>4</sub> ]	420–484	452.3	878 <sup>[e]</sup>	297 <sup>[d]</sup>	82.2 ± 1.6	150.7 ± 1.0	179.5 ± 5.8
[Ph <sub>4</sub> P][B(CN) <sub>4</sub> ]	453–489	470.0	922 <sup>[e]</sup>	308 <sup>[d]</sup>	86.8 ± 1.6	166.6 ± 1.1	212.4 ± 9.2
[PPN][B(CN) <sub>4</sub> ]	463–514	488.2	1346 <sup>[e]</sup>	419 <sup>[d]</sup>	88.2 ± 1.6	165.6 ± 1.0	218.5 ± 10.6
[ <sup>n</sup> Bu <sub>4</sub> N][B(CN) <sub>4</sub> ]	379–437	408.9	678 <sup>[e]</sup>	245 <sup>[d]</sup>	98.9 ± 1.6	184.7 ± 1.4	264.3 ± 16.0
					82.4 ± 1.6	146.6 ± 1.0	173.7 ± 5.5

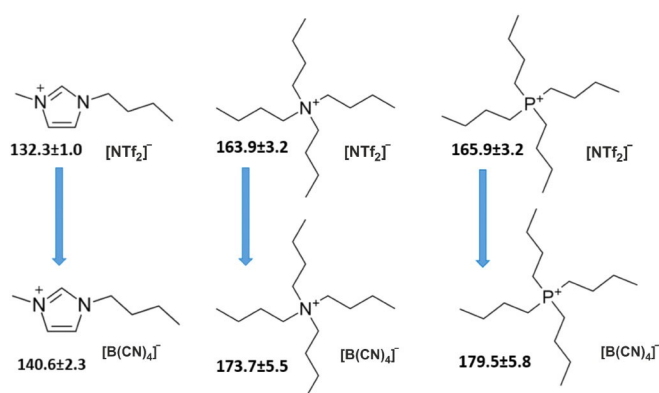
[a] Calculated as explained in the electronic supporting materials. [b] The standard Gibbs energies of vaporisation were evaluated using the calibration coefficient developed in our recent work.<sup>[7]</sup> Uncertainties of vaporisation enthalpy ( $\Delta_i^g H_m^o$ ) and Gibbs free energy of vaporisation ( $\Delta_i^g G_m^o$ ) are the expanded uncertainties (0.95 level of confidence,  $k=2$ ). [c] Adjusted to 298.15 K using the  $\Delta_i^g C_{p,m}^o$  values. Uncertainties in the temperature adjustment of vaporisation enthalpies from  $T_{av}$  to the reference temperature are estimated to account with 20% to the total adjustment. [d] Calculated with  $C_{p,m}^o(l)$  values given in column 4 of this table according to equation developed for the [RMim][NTf<sub>2</sub>] ( $R=$ alkyl):  $\Delta_i^g C_{p,m}^o = C_{p,m}^o(l) \times (-0.26 \pm 0.05) + (68.7 \pm 37.0)$ .<sup>[8]</sup> [e] Calculated with an approach for assessment of  $C_{p,m}^o(l)$  (298.15 K) developed by Ahamadi *et al.* and based on the empirical formula of the ILs.<sup>[9]</sup> [f] Calculated with the  $C_{p,m}^o(l)$  values of this table according to equation developed for the [<sup>n</sup>BuMim][OTf]:  $\Delta_i^g C_{p,m}^o = C_{p,m}^o(l) \times (-0.07 \pm 0.10) - (42.4 \pm 3.6)$ .<sup>[10]</sup> [g] Enthalpy of sublimation. [h] Enthalpy of vaporisation, calculated as explained in the electronic supporting materials.



**Figure 2.** Consistency of experimental vaporisation enthalpies,  $\Delta_i^g H_m^o$  (298.15 K), of alkyl and phenylphosphonium containing ILs (all data are given in  $\text{kJ mol}^{-1}$ )

### 2.3.1 Alkyl and Phenylphosphonium ILs

Let us consider the three structurally similar ionic liquids  $[\text{Bu}_4\text{P}][\text{B}(\text{CN})_4]$ ,  $[\text{Ph}_3(\text{C}_4)\text{P}][\text{B}(\text{CN})_4]$ , and  $[\text{Ph}_4\text{P}][\text{B}(\text{CN})_4]$ , see Figure 2. It is apparent that, with the anion being kept unchanged, the cation has an increasing number of phenyl rings from left to right. Understandably, the vaporisation enthalpy is also qualitatively increasing from the left to the right (see Table 2 and Figure 2). But is this increase quantitatively justified? To prove this, we have performed some group additive calculations shown in Figure 2. Indeed, the enthalpy of vaporisation,  $\Delta_i^g H_m^o$  (298.15 K), of  $[\text{Bu}_4\text{P}][\text{B}(\text{CN})_4]$  divided by 4 delivers a group contribution  $[\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-P}]^+$ . Simply dividing the enthalpy of vaporisation,  $\Delta_i^g H_m^o$  (298.15 K), of  $[\text{Ph}_4\text{P}][\text{B}(\text{CN})_4]$  by 4 provides a group contribution  $[\text{C}_6\text{H}_5\text{-P}]^+$ . Both these fragments are present in the  $[\text{BuPh}_3\text{P}][\text{B}(\text{CN})_4]$ . Hence, we can calculate the “theoretical” vaporisation enthalpy of  $[\text{BuPh}_3\text{P}][\text{B}(\text{CN})_4]$  as a superposition of the  $[\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-P}]^+$  contribution with three  $[\text{C}_6\text{H}_5\text{-P}]^+$ -contributions. The resulting  $\Delta_i^g H_m^o$  (298.15 K) =  $44.9 + 54.6 \times 3 = 208.7 \text{ kJ mol}^{-1}$  agrees with the experimental value  $212.4 \pm 9.2 \text{ kJ mol}^{-1}$ . Such an agreement is evidence of internal consistency of all three vaporisation enthalpies as proved by the relationships between structure and property.



**Figure 3.** Consistency of experimental vaporisation enthalpies,  $\Delta_i^g H_m^o$  (298.15 K), of imidazolium, phosphonium, and ammonium ILs (all data are given in  $\text{kJ mol}^{-1}$ )

### 2.3.2 Alkylimidazolium versus Alkylphosphonium or Alkyl-Ammonium ILs

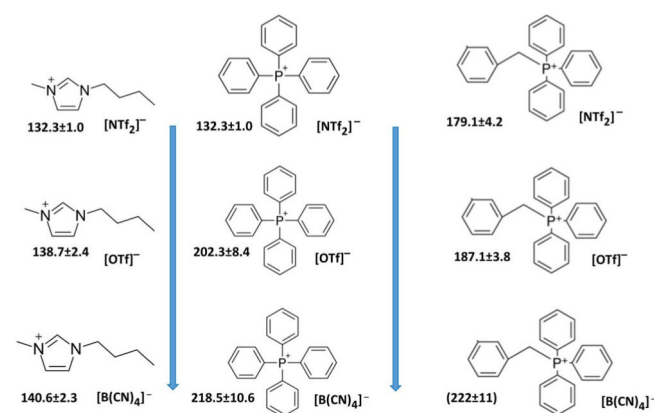
The alkylimidazolium-based ILs with various anions are admittedly the best studied types of ionic liquids. Hence, correlating the new data with well-established data for alkylimidazolium-based ILs could help to reveal a possible inconsistency or systematic error. Reliable vaporisation enthalpies,  $\Delta_i^g H_m^o$  (298.15 K), for  $[\text{BuMIm}][\text{NTf}_2]$  and for  $[\text{BuMIm}][\text{B}(\text{CN})_4]$  were evaluated in our previous studies.<sup>[8,10]</sup> Comparison of results for imidazolium ILs with those for phosphonium and ammonium based ILs is given in Figure 3.

It should be admitted, that accurate quantitative relationships between ILs with the  $[\text{BuMIm}]^+$ , the tetra-alkylsubstituted phosphonium,  $[\text{Bu}_4\text{P}]^+$ , or the ammonium  $[\text{Bu}_4\text{N}]^+$  cation are quite difficult to establish. Nevertheless, even qualitative trends are also valuable to gain consistency of experimental vaporisation enthalpies of imidazolium, phosphonium, and ammonium ILs. As is seen from Figure 3, the vaporisation enthalpy in the ILs with similar shape of the cations increases by exchanging the  $[\text{NTf}_2]^-$  by the  $[\text{B}(\text{CN})_4]^-$  anion in all three series taken for comparison. This qualitative observation endorses the new experimental data.

### 2.3.3 Alkylimidazolium versus Phenylphosphonium ILs

The reliable vaporisation enthalpies,  $\Delta_i^g H_m^o$  (298.15 K), for *n*-butylimidazolium based ionic liquids  $[\text{BuMIm}][\text{NTf}_2]$ ,  $[\text{BuMIm}][\text{B}(\text{CN})_4]$ , and  $[\text{BuMIm}][\text{OTf}]$  were evaluated in our previous studies.<sup>[8,10]</sup> Now they can be correlated with the new data for  $[\text{Ph}_4\text{P}][\text{NTf}_2]$ ,  $[\text{Ph}_4\text{P}][\text{OTf}]$ , and  $[\text{Ph}_4\text{P}][\text{B}(\text{CN})_4]$ , as is shown in Figure 4.

Similar to the trend observed in Figure 3, the vaporisation enthalpies of the tetraphenyl substituted ILs are qualitatively increasing in the sequence from  $[\text{NTf}_2]^-$ ,  $[\text{OTf}]^-$ , and  $[\text{B}(\text{CN})_4]^-$  in agreement with the well-established order for the alkylimidazolium series  $[\text{Ph}_4\text{P}][\text{NTf}_2]$ ,  $[\text{Ph}_4\text{P}][\text{OTf}]$ , and  $[\text{Ph}_4\text{P}][\text{B}(\text{CN})_4]$ . However, for this systems also quantitative comparison is possible, if we



**Figure 4.** Consistency of experimental vaporisation enthalpies,  $\Delta_i^g H_m^o$  (298.15 K), of imidazolium and phenylphosphonium ILs (all data are given in  $\text{kJ mol}^{-1}$ )

directly correlate vaporisation enthalpies,  $\Delta_1^{\circ}H_m^{\circ}$  (298.15 K), of the series  $[\text{Ph}_4\text{P}][\text{Anion}]$  with the series  $[\text{BuMIm}][\text{Anion}]$  as it shown in Figure 5.

### 2.3.4 Tetra-Phenylphosphonium versus Tri-Phenylbenzyl-phosphonium ILS

As it can be seen in Figure 4, the vaporisation enthalpies of  $[\text{Ph}_4\text{P}][\text{NTf}_2]$  and  $[\text{Ph}_3\text{BzP}][\text{NTf}_2]$  are very similar within their experimental uncertainties (see also Table 2). This similarity is quite expected, because these ILS are differing only by the  $\text{CH}_2$  group. From our studies on ILS we know, that the contribution of the  $\text{CH}_2$  group (in the alkyl-chain attached to the imidazolium ring) to the vaporisation enthalpy is around  $4 \text{ kJ mol}^{-1}$ .<sup>[8]</sup> Taking into account that the  $\text{CH}_2$  group in the triphenylbenzyl-phosphonium cation is located between the phosphorus atom and the phenyl group (see Figure 1 and 4), the numerical contribution may be somewhat smaller. Hence, the very close  $\Delta_1^{\circ}H_m^{\circ}$  (298.15 K) values measured for  $[\text{Ph}_4\text{P}][\text{NTf}_2]$  and  $[\text{Ph}_3\text{BzP}][\text{NTf}_2]$  could provide the evidence of data consistency. Regrettably, the large uncertainty ascribed to vaporisation enthalpy of  $[\text{Ph}_4\text{P}][\text{OTf}]$  (the accumulation of uncertainties is due to combination of sublimation and fusion results) does not allow this observation to be confirmed precisely for the pair with  $[\text{Ph}_3\text{BzP}][\text{OTf}]$ . Nevertheless, we propagated the similarity of vaporisation enthalpies of  $[\text{Ph}_4\text{P}][\text{B}(\text{CN})_4]$  and  $[\text{Ph}_3\text{BzP}][\text{B}(\text{CN})_4]$  and calculated the missing value  $\Delta_1^{\circ}H_m^{\circ}$  (298.15 K,  $[\text{Ph}_3\text{BzP}][\text{B}(\text{CN})_4]) = 218.5 + 4 = 222 \pm 11 \text{ kJ mol}^{-1}$  based on the experimental vaporisation enthalpy of the  $[\text{Ph}_4\text{P}][\text{B}(\text{CN})_4]$  given in Table 2.

## 3. Conclusions

The Quartz Crystal Microbalance method (QCM) was used to measure thermodynamic vaporisation data of nine salts, which have melting temperatures between 246.2 K and 585.9 K ( $-27.0$  to  $312.7^\circ\text{C}$ ) and therefore are classified somehow between RTILs, ILS and molten salts. Standard molar enthalpies of vaporisation were derived from vapour pressures measured at different temperatures. These results show, that the ILS with the tetracyanidoborate anion have higher vaporisation enthalpies and lower vapour pressures than most of the common ILS and

may be classified as extremely low-volatile ILS. Using structure-property correlations with the well-established vaporisation enthalpy data of imidazolium based ILS, the internal consistency of the new experimental data was confirmed. These results encourage for the use of these salts to be used as reaction media for a temperature regime higher than that used commonly in organic reactions. This might be useful for solid state chemical applications. Also, the obtained values can be further used for the adjustment of theoretical calculations.

## Experimental Section

### Materials

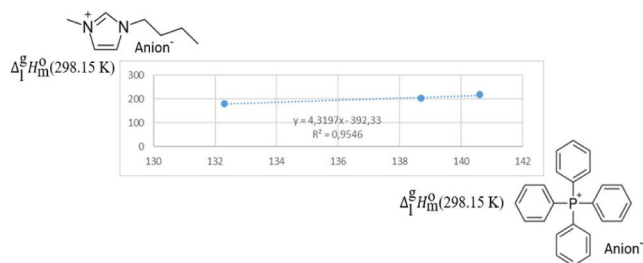
Samples of ILS (see Figure 1) were synthesized as is described in the electronic supporting materials. All ILS were purified by keeping under high vacuum ( $10^{-2}$  mbar) at 333 K for several days. During this process, all volatile impurities or traces of water were removed. Before the beginning of vaporisation experiments, samples were then transferred into the vacuum chamber of vaporisation setup, where the conditioning of the samples was conducted at the highest temperature of the experiment within 12 h. This procedure allowed collecting of the sufficient amount of the vaporized IL required for the ATR-IR spectroscopy analysis.

### Differential Scanning Calorimetry (DSC)

The thermal behaviour of crystalline samples including melting temperatures was studied with a commercial DSC Mettler Toledo DSC 822e coupled with Huber TC100MT cooler. A sample was placed in the standard non-pinned aluminium pan of 40  $\mu\text{l}$  volume. Pan and sample were weighted with a Sartorius MSE3.6P-000-DM microbalance with the standard uncertainty of  $5 \cdot 10^{-6}$  g. In the first DSC run the sample was heated with a rate of  $10 \text{ K min}^{-1}$  to 398 K ( $\sim 30$  K above the melting temperature provided by the supplier) and then cooled down to 298 K, also with the rate of  $10 \text{ K min}^{-1}$ . This procedure provided sufficient contact between the sample and the bottom of the pan. The DSC experiments were repeated three times. The calibration of the DSC was checked with the melting point of a reference indium sample. The twice standard deviation of the melting temperature in the test measurements for the reference compound was  $\pm 0.3$  K. Details are reported elsewhere.<sup>[11]</sup>

### Quartz Crystal Microbalance (QCM)

Vapour pressures and molar enthalpies of vaporisation of ILS were measured using the QCM method.<sup>[12]</sup> The IL sample was placed in an open cavity (Langmuir evaporation) inside the thermostated block and exposed to high vacuum ( $10^{-5}$  Pa) with the entire open surface of the loaded in the cavity compound. The QCM-sensor was mounted directly above the measuring cavity with the sample. During the evaporation in the high vacuum, a certain amount of the sample was condensed on the quartz crystal surface. The change of the vibrational frequency was recorded and directly related to the mass deposition on the QCM. The enthalpy of vaporisation (see Table 1) was derived from the temperature dependence of the mass loss according to the Clausius-Clapeyron equation. The primary experimental results of the QCM studies are shown in Table S1 in the Supporting Information. The absence of decomposition of the IL under experimental conditions was controlled by using spectroscopy. The residual amount of IL in the cavity, as well as the IL deposit on QCM were analysed by ATR-IR



**Figure 5.** Correlation of vaporisation enthalpies,  $\Delta_1^{\circ}H_m^{\circ}$  (298.15 K), of imidazolium and tetra-phenylphosphonium ILS (all data are given in  $\text{kJ mol}^{-1}$ ). The robust correlation with the  $R^2 = 0.955$  is an evidence of the internal consistency of our new data for the series  $[\text{Ph}_4\text{P}][\text{Anion}]$  (see Table 2).

spectroscopy. No changes in the spectra have been detected, as can be seen in Figures S1 to S6 of the Supporting Information.

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## Conflict of Interest

The authors declare no conflict of interest.

**Keywords:** ionic liquids · vapour pressure · aporisation enthalpies · structure-property relationships · thermodynamics

- [1] a) F. Endres, S. Zein El Abedin, *Phys. Chem. Chem. Phys.* **2006**, *8*, 2101–2116; b) S. A. Forsyth, J. M. Pringle, D. R. MacFarlane, *Aust. J. Chem.* **2004**, *57*, 113–119; c) M. Freemantle, *An Introduction to Ionic Liquids*, The Royal Society of Chemistry, **2009**; d) J. P. Hallett, T. Welton, *Chem. Rev.* **2011**, *111*, 3508–3576; e) N. V. Plechkova, K. R. Seddon, *Chem. Soc. Rev.* **2008**, *37*, 123–150; f) P. Wasserscheid, W. Keim, *Angew. Chem. Int. Ed.* **2000**, *39*, 3772–3789; *Angew. Chem.* **2000**, *112*, 3926–3945; g) T. Welton, *Chem. Rev.* **1999**, *99*, 2071–2083; h) T. Welton, *Biophys. Rev. Lett.* **2018**, *10*, 691–706.
- [2] a) A. P. Abbott, G. Capper, B. G. Swain, D. A. Wheeler, *Transactions of the IMF* **2005**, *83*, 51–53; b) A. P. Abbott, G. Frisch, J. Hartley, K. S. Ryder, *Green Chem.* **2011**, *13*, 471–481; c) M. J. Earle, K. R. Seddon, *Pure Appl. Chem.* **2000**, *72*, 1391; d) K. Ghandi, *Green Sustainable Chem.* **2014**, *4*, 44–53; e) A. Hinsch, S. Behrens, M. Berginc, H. Bonnemann, H. Brandt, A. Drewitz, F. Einsele, D. Fassler, D. Gerhard, H. Gores, R. Haag, T. Herzig, S. Himmler, G. Khelashvili, D. Koch, G. Nazmutdinova, U. Opara-Krasovec, P. Putyra, U. Rau, R. Sastrawan, T. Schauer, C. Schreiner, S. Sensfuss, C. Siegers, K. Skupien, P. Wachter, J. Walter, P. Wasserscheid, U. Wurfel, M. Zistler, *Prog. Photovoltaics* **2008**, *16*, 489–501; f) H. Olivier-Bourbigou, L. Magna, *J. Mol. Catal. A* **2002**, *182–183*, 419–437; g) R. Sheldon, *Chem. Commun.* **2001**, 2399–2407; h) P. Wasserscheid, T. Welton, *Ionic liquids in synthesis*, 2nd ed., Wiley-VCH John Wiley, Weinheim; Chichester, **2008**.
- [3] P. Walden, *Bull. Acad. Imp. Sci. St.-Petersbourg* **1914**, *8*, 405–422.
- [4] G. Boeck, T. Peppel, D. Selent, A. Schulz, *Nachr. Chem.* **2017**, *65*, 1030–1033.
- [5] a) A. Michaelis, H. v. Soden, *Liebigs Ann. Chem.* **1885**, *229*, 295–334; b) A. Flemming, M. Hoffmann, M. Köckerling, *Z. Anorg. Allg. Chem.* **2010**, *636*, 562–568.
- [6] A. Siegesmund, A. Topp, C. Nitschke, M. Köckerling, *ChemistrySelect* **2017**, *2*, 11328–11335.
- [7] D. H. Zaitsau, A. V. Yermalayeu, V. N. Emel'yanenko, S. Butler, T. Schubert, S. P. Verevkin, *J. Phys. Chem. B* **2016**, *120*, 7949–7957.
- [8] S. P. Verevkin, D. H. Zaitsau, V. N. Emel'yanenko, A. V. Yermalayeu, C. Schick, H. Liu, E. J. Maginn, S. Bulut, I. Krossing, R. Kalb, *J. Phys. Chem. B*, **2013**, *117*, 6473–6486.
- [9] A. Ahmadi, R. Haghbakhsh, S. Raeissi, V. Hemmati, *Fluid Phase Equilib.* **2015**, *403*, 95–103.
- [10] D. H. Zaitsau, K. Pohako-Esko, S. Arlt, V. N. Emel'yanenko, P. S. Schulz, P. Wasserscheid, A. Schulz, S. P. Verevkin, *J. Mol. Liq.* **2017**, *248*, 86–90.
- [11] S. P. Verevkin, R. V. Ralys, D. H. Zaitsau, V. N. Emel'yanenko, C. Schick, *Thermochim. Acta* **2012**, *538*, 55–62.
- [12] S. P. Verevkin, D. H. Zaitsau, V. N. Emel'yanenko, A. Heintz, *J. Phys. Chem. B*, **2011**, *115*, 12889–12895.

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