

Volatility of molten salts [Ph₄P][NTf₂] and Cs[NTf₂]

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The two ionic compounds [Ph₄P][NTf₂] and Cs[NTf₂] were qualified to be suitable liquid materials for different high temperature applications. Development and optimization of these application techniques require knowledge of the thermo-

dynamic properties of vaporization. Vapor pressures and vaporization enthalpies have been measured by using quartz-crystal microbalance. Solubility parameters and miscibility of ionic liquids in practically relevant solvents were assessed.

1. Introduction

ILs are a neoteric class of materials that consist entirely of anions and cations, with melting temperatures being defined arbitrarily a value below 100 °C. From the late 1990s, research on ionic liquids (ILs) received profound and increasing scientific attention. The main reason for this can be unusual (compared to the common salts) physico-chemical properties such as a wide range of liquid states at moderate temperatures, low viscosity, special coordination behavior and ionic conductivity. Due to the structural diversity of ILs, these properties can be deliberately adapted for different task-specific applications by combining suitable cations and anions.^[1] Most of these applications are based on extremely low vapor pressure < 10⁻³ Pa, even at elevated temperatures, for example as reaction media or heat transfer media, in separation processes, in high temperature catalysis, etc.^[2]

This work is a continuation of our previous study of two ionic compounds [Ph₄P][NTf₂] and Cs[NTf₂], which were qualified to be a suitable liquid material for different high temperature applications.^[3] With melting points above 100 °C ([Ph₄P][NTf₂] with 134 °C and Cs[NTf₂] with 125 °C), these salts do not correspond to the arbitrary but conventional definition of ionic liquids. In order to avoid confusion with the classification of


these ionic compounds as molten salts or ionic liquids, we have decided within the scope of this work to define both compounds as ionic liquids. Both compounds [Ph₄P][NTf₂] and Cs[NTf₂] are highly thermally stable and very interesting for the immobilization of catalysts that are required for chemical reactions at elevated temperatures up to 350 °C, where common ILs already tend to decompose. This is especially important in the context of hydrogen storage with the liquid organic hydrogen carriers (LOHC), where the dehydrogenation reactions still occur at temperature not too far from 300 °C.^[4,5] For example, the thermally stable salts were successfully used for the dehydrogenation of indoline to indole with homogeneous Ir catalysts immobilized in the mixture of [Ph₄P][NTf₂] and Cs[NTf₂].^[6] Nevertheless, the sufficient thermal stability of ionic liquids is required for processes involving LOHC. The thermal stability of ionic liquids is often defined as the onset temperature (T_{onset}) of the beginning of the measurable mass loss during the thermogravimetric heating of an IL sample. This definition is not always correct, because this temperature T_{onset} depends on the heating rate, the sample amount, on the size and material of the sample pan, the flow rate and the type of the carrier gas. Usually the T_{onset} gives an overestimation of the thermal stability.^[7,8] In this context, a "maximum operation temperature" is a more objective indicator for thermal stability and volatility of an IL. The latter corresponds to the pre-defined chemical rate, commonly 1% mass loss per year.^[7]


Regardless of the definition, at the elevated temperatures the real mass loss of the thermally stressed IL sample is generally stipulated by two simultaneous processes: evaporation and thermal degradation. For practical IL applications, however, the operating temperature must be set as low as possible in order to avoid possible decomposition. Therefore, the mass loss due solely to physical evaporation becomes a critical factor in the long-term use of IL in industry. For example, for applications where a gas flows through an IL, e.g. for regeneration of ILs used for extraction or absorption, or for solid catalyst supports coated with IL (like in the SILP or SCILL concept^[9,10]), the evaporation has to be taken into account and might become the limiting factor for the maximal operation temperature. Admittedly, the evaporation is determined by the absolute vapor pressure values. Vapor pressures are also involved in the T_{onset} , maximal operation temperature, as well as for the mass-transfer calculations.^[3,7,8] Preliminary results on the


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volatility of the ionic liquids $[\text{Ph}_4\text{P}][\text{NTf}_2]$ and $\text{Cs}[\text{NTf}_2]$ (see Figure 1), have been already reported.^[3]

In this paper we report the precise absolute vapor pressures and enthalpies of vaporization, $\Delta_f^{\circ}H_m^{\circ}$, of $[\text{Ph}_4\text{P}][\text{NTf}_2]$ and $\text{Cs}[\text{NTf}_2]$, which were measured using the quartz-crystal microbalance (QCM) method. These values have been used for qualitative assessment solubilities of ionic compounds in common ionic liquids of practical importance. This is essential to their use as a solvent to immobilize catalysts for the processes of chemical hydrogen storage.

Experimental Section

Materials

Samples of the ionic liquids $[\text{Ph}_4\text{P}][\text{NTf}_2]$ and $\text{Cs}[\text{NTf}_2]$ (see Figure 1) were synthesized as it described in the electronic supporting materials. Both ionic liquids were first purified by keeping under high vacuum conditions (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 vaporization 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 ionic liquids required for the ATR-IR spectroscopy analysis.

Isothermal TGA Appraisal of the Vaporization Enthalpy

Thermal behaviour of the $[\text{Ph}_4\text{P}][\text{NTf}_2]$ was studied with the Perkin Elmer Pyris 6 TGA setup in order to assess the range of volatility and thermal stability of the sample. For this purpose, a plane crucible made of Pt with about 70 mg of the sample was heated at a nitrogen flow rate of $200 \text{ ml} \cdot \text{min}^{-1}$ with a ramp of $10 \text{ K} \cdot \text{min}^{-1}$. Vaporization enthalpy measurements were performed in the

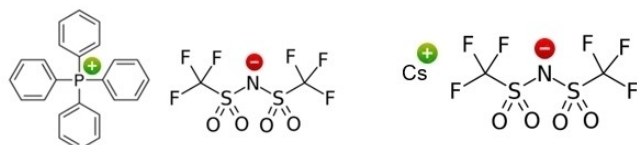


Figure 1. Structures of compounds studied in this work: $[\text{Ph}_4\text{P}][\text{NTf}_2]$ (left) and $\text{Cs}[\text{NTf}_2]$ (right)

isothermal steps. The TGA curves for $[\text{Ph}_4\text{P}][\text{NTf}_2]$ were measured in the temperature range 578–632 K. Measurements of the mass loss rate dm/dt in a typical experiment were performed in a few consequent series with the increasing temperature steps. The determination of the rate of mass loss in each series was carried out in steps consisting of 6 to 8 temperature points. The reproducibility of the results was confirmed by a series of several runs. The enthalpy of vaporization (see Table 1) was derived from the temperature dependence of the mass loss $r=dm/dt$ according to the Clausius-Clapeyron equation. The detailed procedure was already described elsewhere.^[11]

Quartz Crystal Microbalance (QCM)

Vapor pressures and molar enthalpies of vaporization of $[\text{Ph}_4\text{P}][\text{NTf}_2]$ and $\text{Cs}[\text{NTf}_2]$, were measured by using the QCM method.^[12] An IL sample was placed in an open cavity (Langmuir evaporation) inside the thermostatted block and exposed to a 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 a high vacuum the sample condenses on the quartz crystal surface. The change of the vibrational frequency Δf was recorded. It is directly related to the mass deposition Δm on the QCM according to the Sauerbrey equation:^[13]

$$\Delta f = -C \times f^2 \times \Delta m \times S_c^{-1} \quad (1)$$

where f is the fundamental frequency of the crystal (6 MHz in this case) with $\Delta f \ll f$, S_c is the surface of the crystal, and C is a constant.^[13] The measured frequency change rates (df/dt) is used for calculation of absolute vapor pressures p_s according to equation:

$$p_i = K' \frac{df}{dt} \sqrt{\frac{T}{M}} \quad (2)$$

where the $K' = (9.5 \pm 1.1) \cdot 10^{-6} \text{ Pa} \cdot \text{s} \cdot \text{kg}^{1/2} \cdot \text{Hz}^{-1} \cdot \text{K}^{-1/2} \cdot \text{mol}^{-1/2}$ ^[14] is the empirical calibration constant including all parameters involved in Eq. 1, as well as all parameters specific to the device geometry. The calibration of the set-up was carried out using the vapor pressure data of imidazolium and pyridinium series of ionic liquids, where reliable experimental data are available from the literature. Standard molar enthalpie of vaporization, $\Delta_f^{\circ}H_m^{\circ}(T_0)$, were calculated as follows:

Table 1. Thermodynamics of vaporization/sublimation of $[\text{Ph}_4\text{P}][\text{NTf}_2]$ and $\text{Cs}[\text{NTf}_2]$ derived from QCM results.

Compound	Method	T-range [K]	T_{av}	$\Delta_f^{\circ}H_m^{\circ}(T_{av})$ [kJ·mol ⁻¹]	$\Delta_f^{\circ}G_m^{\circ}(T_{av})$ ^[a]	$\Delta_f^{\circ}C_{p,m}^{\circ}$ ^[b] [J·K ⁻¹ ·mol ⁻¹]	$\Delta_f^{\circ}H_m^{\circ}(298.15 \text{ K})$ ^[c] [kJ·mol ⁻¹]
1	2	3	4	5	6	7	8
[[Ph ₄ P][NTf ₂]	TGA	380–470	425	135	–	-130	(152)
	TGA	578–632	605.9	162 ± 10	–	–	(202 ± 13)
	QCM	413–465	438.9	162.4 ± 1.0	87.7 ± 1.3	–	180.7 ± 3.9
[Cs][NTf ₂]	TGA	380–470	425	125	–	-80	(135)
	QCM	394–484	434.7	148.2 ± 1.0	82.4 ± 1.3	–	159.1 ± 2.4

[a] The standard Gibbs energies of vaporization were evaluated using the calibration coefficient developed in our recent work^[14]. Uncertainties of vaporization enthalpy ($\Delta_f^{\circ}H_m^{\circ}$) and Gibbs free energy of vaporization ($\Delta_f^{\circ}G_m^{\circ}$) are the expanded uncertainties (0.95 level of confidence, $k=2$). [b] Calculated according to Eq. 7. [c] Adjusted to 298.15 K using the $\Delta_f^{\circ}C_{p,m}^{\circ}$ -values from column 7. Uncertainties in the temperature adjustment of vaporization enthalpies from T_{av} to the reference temperature are estimated to account with 20% to the total adjustment. Values given in brackets were not taken into account. Values given in italic are recommended for the thermochemical calculations.

$$\ln\left(\frac{df}{dt}\sqrt{T}\right) = A' - \frac{\Delta_1^{\circ}H_m^{\circ}(T_0) - \Delta_1^{\circ}C_{p,m}^{\circ}T_0}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right) + \frac{\Delta_1^{\circ}C_{p,m}^{\circ}}{R}\ln\left(\frac{T}{T_0}\right) \quad (3)$$

where T_0 is an arbitrarily chosen reference temperature (T_0 is an average temperature of the experimental range of the QCM study) and A' is the empirical constant.

The value $\Delta_1^{\circ}C_{p,m}^{\circ} = C_{p,m}^{\circ}(\text{g}) - C_{p,m}^{\circ}(\text{l})$ is the difference between the molar heat capacities of the gaseous $C_{p,m}^{\circ}(\text{g})$ and the liquid phase $C_{p,m}^{\circ}(\text{l})$ respectively. The vaporization enthalpies $\Delta_1^{\circ}H_m^{\circ}(T)$ at any desired temperature are calculated according to the Kirchoff's equation:

$$\Delta_1^{\circ}H_m^{\circ}(T) = \Delta_1^{\circ}H_m^{\circ}(T_0) + \Delta_1^{\circ}C_{p,m}^{\circ}(T - T_0) \quad (4)$$

A typical experiment was carried out in several consecutive series with increasing and decreasing temperature steps. Each series included 7 to 11 temperature points to determine the rate of mass loss. Such a procedure enabled the detection of possible sample degradation during the frequency loss rate (df/dt) measurements. The reproducibility of the results was determined in a series of randomly performed test runs. The study was considered to be complete when the $\Delta_1^{\circ}H_m^{\circ}(T)$ -values derived from the temperature-dependent rates (df/dt) achieved the uncertainty level of $\pm 1 \text{ kJ}\cdot\text{mol}^{-1}$. The primary experimental results of the QCM studies are shown in Table S2 in the Supporting Information. The absence of decomposition of 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 analyzed by ATR-IR spectroscopy. No changes in the spectra have been detected, as can be seen in Figures S1 to S2 of the Supporting Information.

2. Results and Discussion

2.1. Absolute Vapor Pressures as Determined by QCM

One of the key advantages that aprotic ILs have often highlighted is that they are considered non-volatile at ambient temperatures. However, as the temperature increases, the volatility of an IL also gradually increases, and at the elevated temperatures typically used in industrial applications, the volatility could already be significant ($> 1 \text{ Pa}$). The volatility is usually related to vapor pressure. The absolute vapor pressures of the $[\text{Ph}_4\text{P}][\text{NTf}_2]$ were measured between 413 K and 473 K. The absolute vapor pressures of the $\text{Cs}[\text{NTf}_2]$ were measured between 394 K and 484 K. The comparison of the volatility of differently structured ILs is important for numerous catalytic applications of SILP^[9] and SCILL.^[10] For practical purpose, the vapor pressure of the IL at a certain temperature is decisive for the mass loss from the liquid phase^[9] and from the surface of a solid catalyst.^[10] The frequency changes rates (df/dt) measured in this work by using the QCM were used for calculating the vapor pressures p_i of $[\text{Ph}_4\text{P}][\text{NTf}_2]$ and $\text{Cs}[\text{NTf}_2]$, according to Eq. 2 (see Table S1), which are then compared with data reported for the most carefully studied $[\text{C}_n\text{C}_1\text{Im}][\text{NTf}_2]$ family (Figure 2). The vapor pressures of the $[\text{Ph}_4\text{P}][\text{NTf}_2]$ and $\text{Cs}[\text{NTf}_2]$, are significantly lower than those of the $[\text{C}_n\text{C}_1\text{Im}][\text{NTf}_2]$ series.

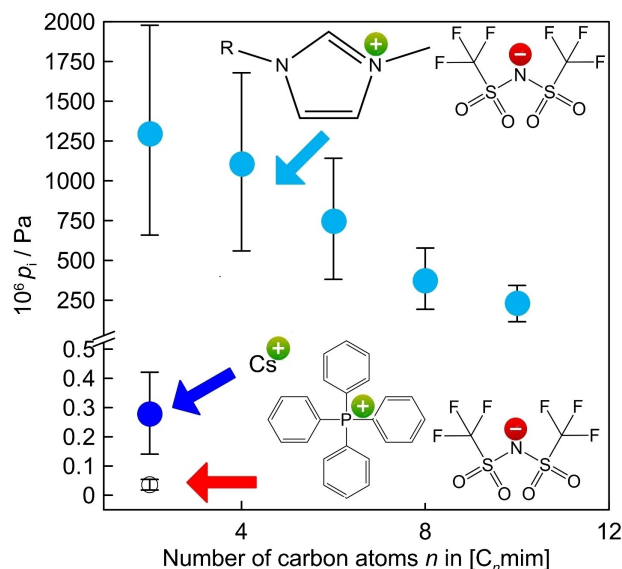


Figure 2. Chain-length dependence of absolute vapor pressures at $T = 423.15 \text{ K}$ for homologous series $[\text{C}_n\text{C}_1\text{Im}][\text{NTf}_2]$ (●) from^[15], vapor pressure of the $[\text{Ph}_4\text{P}][\text{NTf}_2]$ (□) and $\text{Cs}[\text{NTf}_2]$ (●).

From this point of view, the use of the $[\text{Ph}_4\text{P}][\text{NTf}_2]$ and $\text{Cs}[\text{NTf}_2]$, for example in catalytic applications is advantageous, if their estimated thermal stability at the level of 573 K is also taken into account.^[3]

Admittedly, the volatility is directly related to the vapor pressure according to the following general thermodynamic equation:

$$\ln p_i = -\Delta_1^{\circ}G_m^{\circ}(T)/RT \quad (5)$$

Surprisingly, the $\Delta_1^{\circ}G_m^{\circ}(T_{av})$ -values as-derived from the QCM vapor pressure measurements for $[\text{Ph}_4\text{P}][\text{NTf}_2]$ and $\text{Cs}[\text{NTf}_2]$ are not much different (see Table 1), even taking into account slightly different average temperatures. This observation could simplify technical calculations of vapor pressures for the ionic liquids of similar structures at different and technically relevant temperatures. For generalization, however, further observations of the absolute ILs vapor pressures and $\Delta_1^{\circ}G_m^{\circ}(T_{av})$ -values are required.

2.2. Experimental Vaporization Enthalpies of $[\text{Ph}_4\text{P}][\text{NTf}_2]$ and $\text{Cs}[\text{NTf}_2]$

The standard molar enthalpies of vaporization $\Delta_1^{\circ}H_m^{\circ}(T_{av})$ were derived for $[\text{Ph}_4\text{P}][\text{NTf}_2]$ and $\text{Cs}[\text{NTf}_2]$ from vapor pressures temperature dependences are referenced to average temperatures T_{av} . These results are presented in Table 1, column 4. Conventionally, experimental vaporization enthalpies are adjusted to any common temperature (e.g. the reference temperature $T = 298.15 \text{ K}$) in order to compare or reveal structure-property relationships. The vaporization enthalpy at the reference temperature, $\Delta_1^{\circ}H_m^{\circ}(298.15 \text{ K})$, was calculated according to the Kirchoff's equation:

$$\Delta_1^{\circ}H_m^{\circ}(298.15\text{ K}) = \Delta_1^{\circ}H_m^{\circ}(T_{av}) + \Delta C_{p,m}^{\circ} \times (T_{av} - 298.15\text{ K}) \quad (6)$$

The value $\Delta_1^{\circ}C_{p,m}^{\circ} = C_{p,m}^{\circ}(\text{g}) - C_{p,m}^{\circ}(\text{liq})$ is the difference between the molar heat capacities of the gaseous $C_{p,m}^{\circ}(\text{g})$ and the liquid phase $C_{p,m}^{\circ}(\text{liq})$, respectively.

Unfortunately, information on the $C_{p,m}^{\circ}(\text{liq})$ -values for the $[\text{Ph}_4\text{P}][\text{NTf}_2]$ and $\text{Cs}[\text{NTf}_2]$ is absent. Moreover, for the phosphorus containing ILs, only for $[\text{P}_{6,6,6,14}][\text{NTf}_2]$ the experimental value $C_{p,m}^{\circ}(l) = 1299\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ was reported by Ferreira *et al.*^[16] For this reason we used this experimental value to develop a simple group additivity method suitable for evaluating the heat capacities of liquids for other ILs. In this procedure we endorse and follow the well-established group-contribution method by Chickos *et al.*^[17] and we use their parameters for hydrocarbon groups $(\text{CH}_3) = 34.9\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ and $(\text{CH}_2) = 31.9\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ included into the cation alkyl-chains. A subtraction of $4\times(\text{CH}_3)$ and $29\times(\text{CH}_2)$ contributions from the experimental value $C_{p,m}^{\circ}(l) = 1299\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ provides a group contribution for the core $[\text{P}_{x,x,x,x}][\text{NTf}_2]$ specific for the phosphonium based cation connected to the $[\text{NTf}_2]$ anion. With help of this core contribution, the liquid phase heat capacity of $[\text{Ph}_4\text{P}][\text{NTf}_2]$ was calculated by the summation of $[\text{P}_{x,x,x,x}][\text{NTf}_2]$ -value with an appropriate number of $(\text{C}_6\text{H}) = 21.8\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ and $(\text{C}_6\text{R}) = 15.3\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ contributions which form the phenyl rings around of the phosphorus atom on the $[\text{Ph}_4\text{P}][\text{NTf}_2]$. The estimated value $C_{p,m}^{\circ}(l) = 763\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ (see Table 2) was used to obtain the value $\Delta_1^{\circ}C_{p,m}^{\circ}$ required for the temperature adjustment according to the Kirchhoff's equation Eq. 6 as follows.

In our recent work on the $[\text{C}_n\text{mim}][\text{NTf}_2]$ series the experimental $\Delta_1^{\circ}C_{p,m}^{\circ}$ -values were correlated with the experimental $C_{p,m}^{\circ}(l, 298.15\text{ K})$ providing empirical equation for the $[\text{NTf}_2]$ -family:

$$\Delta_1^{\circ}C_{p,m}^{\circ}/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = C_{p,m}^{\circ}(l, 298.15\text{ K}) \times (-0.26 \pm 0.05) + (69 \pm 37) \quad (7)$$

Table 2. Compilation of data on molar heat capacities $C_{p,m}^{\circ}$ and heat capacity differences $\Delta_1^{\circ}C_{p,m}^{\circ}$ (in $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$) at $T = 298.15\text{ K}$ for the ionic liquids under study

IL	$C_{p,m}^{\circ}(\text{liq})^{[a]}$	$-\Delta_1^{\circ}C_{p,m}^{\circ}^{[b]}$
$[\text{Ph}_4\text{P}][\text{NTf}_2]$	763	130
$\text{Cs}[\text{NTf}_2]$	573 ^[c]	80

[a] Calculated as described in the text. [b] Calculated according to Eq. 7. [c] Assessed according to the empirical procedure suggested by Ahmadi *et al.*^[18]

Table 3. Calculations of solubility parameters δ_2 of $[\text{Ph}_4\text{P}][\text{NTf}_2]$ and $\text{Cs}[\text{NTf}_2]$.

IL	MW/ [$\text{g}\cdot\text{mol}^{-1}$]	$\rho_{473\text{ K}}^*$ / [$\text{g}\cdot\text{cm}^{-3}$]	V_2^* / [$\text{cm}^3\cdot\text{mol}^{-1}$]	$\Delta_1^{\circ}H_m^{\circ}(298.15\text{ K})^{[a]}$ / [$\text{kJ}\cdot\text{mol}^{-1}$]	$\delta_2/\text{MPa}^{0.5}$
$[\text{Ph}_4\text{P}][\text{NTf}_2]$	619.2	1.2 [3]	516.0	180.7 ± 3.9	18.6
$\text{Cs}[\text{NTf}_2]$	413.0	2.2 [3]	187.7	159.1 ± 2.4	28.9

We assumed that the Eq. 7 developed for the $[\text{C}_n\text{mim}][\text{NTf}_2]$ family is also valid for the ionic liquids with the phosphonium containing in the cation and calculated the required $\Delta_1^{\circ}C_{p,m}^{\circ}$ value for the $[\text{Ph}_4\text{P}][\text{NTf}_2]$ (see Table 2).

The standard molar enthalpies of vaporization $\Delta_1^{\circ}H_m^{\circ}(T_{av})$ derived for $[\text{Ph}_4\text{P}][\text{NTf}_2]$ and $\text{Cs}[\text{NTf}_2]$ and adjusted to the reference temperature $T = 298.15\text{ K}$ are given in Table 1, last column.

The vaporization enthalpies of $[\text{Ph}_4\text{P}][\text{NTf}_2]$ and $\text{Cs}[\text{NTf}_2]$ reported in our previous work^[3] should be considered rather as the fitting parameters for the mass loss approximations derived from the TGA measurements. The vaporization enthalpy of $[\text{Ph}_4\text{P}][\text{NTf}_2]$ derived from the TGA measurements in this work is in fair agreement with the result from the QCM study. However, the TGA study on the extremely low volatile ionic liquids $[\text{Ph}_4\text{P}][\text{NTf}_2]$ demonstrates that this method needs further developments towards such unusual type of compounds.

2.3. Solubility Parameters of $[\text{Ph}_4\text{P}][\text{NTf}_2]$ and $[\text{Cs}][\text{NTf}_2]$

Surprisingly, in our previous work it was observed that the inorganic salt $\text{Cs}[\text{NTf}_2]$ and bulky organic imide salts $[\text{Ph}_4\text{P}][\text{NTf}_2]$ show excellent miscibility and eutectic behavior.^[3] This observation may open new routes to salt mixtures of new properties. In the special case of binary $\text{Cs}[\text{NTf}_2]$ - $[\text{Ph}_4\text{P}][\text{NTf}_2]$ mixtures this approach lowers the melting point of $[\text{Ph}_4\text{P}][\text{NTf}_2]$ by around 40°C and brings the melting point below 100°C .^[3] The mutual solubility or miscibility of compounds is of practical interest for various applications. In this work we decided to test an approach based on vaporization enthalpies to get a quick assessment of the solubility.

Vaporization enthalpies, $\Delta_1^{\circ}H_m^{\circ}(298.15\text{ K})$, of $[\text{Ph}_4\text{P}][\text{NTf}_2]$ and $\text{Cs}[\text{NTf}_2]$ derived in this work (see Table 1) we used for the estimation of total solubility parameter (δ_T) by using Eq. 8^[19]:

$$\delta_T = [(\Delta_1^{\circ}H_m^{\circ} - RT)/V_m]^{0.5}, \quad (8)$$

where R is the ideal gas constant, T is the temperature, and V_m is the molar volume. Experimental ILs densities required for calculations of V_m are given in Table 3.

Solubility parameters δ_1 (subscript 1 is reference to a solute) and δ_2 (subscript 2 is reference to a solvent) describe the mutual miscibility of 1 and 2. According to Hildebrand's theory, materials with similar values of δ are likely to be qualitatively miscible. Quantitatively miscibility is represented over a Flory-Huggins interaction parameters, χ_{21} at infinite dilution:^[19,20]

$$\chi_{21} = \frac{V_2^* (\delta_2 - \delta_1)^2}{RT} \quad (9)$$

where δ_2 is the solubility parameter of the particular IL and δ_1 is the solubility parameter of the solute of interest, R denotes the universal gas constant, T is the temperature, V_2^* is the molar volume of the IL. Solubility parameters δ_2 of [Ph₄P][NTf₂] and Cs[NTf₂] at $T=298.15$ K ($p^\circ=0.1$ MPa) were calculated according to Eq. 8 (see Table 3). Uncertainties of δ_2 -values are generally related to the uncertainties of vaporization enthalpies and they are assessed to be at the level of 0.5 MPa^{0.5}. Solubility parameters for the different solutes, δ_1 , are given in Table 4, column 5.

The Flory–Huggins interaction parameters, χ_{21} , calculated for different salts and ionic liquids in [Ph₄P][NTf₂] according to Eq. 9 are collected in Table 4.

To get a deeper insight, we additionally considered Li[NTf₂] and the [C_nmim][NTf₂]-series as practically relevant solutes in order to assess their miscibility with [Ph₄P][NTf₂]. The results estimated in Table 4 together with our practical qualitative experience lead to the conclusion that values of χ_{21} for Cs[NTf₂] and Li[NTf₂] are quite similar and apparently the level of χ_{21} -values indicates a sufficient solubility of ionic compounds in [Ph₄P][NTf₂]. It is also evident that the representatives of the [C_nmim][NTf₂] series show a better solubility in [Ph₄P][NTf₂] than the ionic liquids which carry the same anion. Also, the longer the chain in the [C_nmim][NTf₂] series, the better the solubility in [Ph₄P][NTf₂] (see decreasing with the chain length χ_{21} -values in Table 4). As can be seen in Table 4, the anions influence the solubility considerably. The solubilities of ILs based on imidazo-

lium cation with an anion other than [NTf₂] are lower (χ_{21} -values are at the level of the ionic liquids), but still sufficient.

The solubility of salts in ionic liquids is of particular importance for batteries. It is well-known,^[22] that lithium salts used in batteries have poor solubility in many common ILs, *e.g.* such as [C_nmim][NTf₂]. In the context of this work, we calculated χ_{21} -values for Cs[NTf₂] and Li[NTf₂] in imidazolium based ionic liquids (see Table 5).

Results given in Table 5 indicate that miscibilities of Cs[NTf₂] and Li[NTf₂] in imidazolium based ionic liquids are quite comparable. This observation is consonant with the experimental results: for Cs[NTf₂] the solubility in [C₂mim][NTf₂] is 0.3 mole fraction,^[23] for Li[NTf₂] the solubility in C₂mim[NTf₂] is 0.4 mole fraction.^[22,23] Also the longer the chain in the [C_nmim][NTf₂] series, the worse the solubility of Cs[NTf₂] and Li[NTf₂] in [C_nmim][NTf₂] (see increasing with the chain length χ_{21} -values in Table 5) and such a behavior is quite reasonable taking into account decreasing of the Coulomb forces with the longer chain length.

Lithium salt solutions in ionic liquids that contain the thiocyanate anion [SCN], in contrast to ILs with the [NTf₂] anion, can be prepared at concentrations as high as 1.3 M.^[22] This experimental finding is in agreement with the trend calculated with the χ_{21} -values. Indeed, for [C₄mim][SCN] $\chi_{21}=0.1$ (solubility 1.3 molar fraction^[22]) and for [C₂mim][NTf₂] $\chi_{21}=6.1$ (solubility 0.4 molar fraction^[22,23]). Such a reasonable agreement of theoretical solubility trends and demanding experimental determinations can be considered as a general validation of the $\Delta_1^g H_m^\circ$ (298.15 K)-based prediction method. This simple method is very useful for a quick qualitative assessment of the liquid-liquid equilibrium systems.

Table 4. Calculations of solubility parameter χ_{21} of different ionic compounds in [Ph₄P][NTf₂]

IL	MW/ g · mol ⁻¹	$\rho_{293K}^{(a)}$ g · cm ⁻³	$\Delta_1^g H_m^\circ$ (298.15 K) ^(b) kJ · mol ⁻¹	δ_1 / ^(c) MPa ^{0.5}	χ_{21} ^(d)
Li[NTf ₂]	287.0	1.70	151.4 ^(e)	29.7	25.7
Cs[NTf ₂]	413.0	2.20 ^(f)	159.1 ^(g)	28.9	22.1
C ₂ mim[NTf ₂]	391.3	1.52	127.7	22.1	2.5
C ₄ mim[NTf ₂]	419.4	1.44	134.9	21.3	1.6
C ₆ mim[NTf ₂]	447.4	1.37	140.1	20.5	0.8
C ₄ mim[PF ₆]	284.2	1.37	146.5	26.3	12.6
C ₄ mim[BF ₄]	226.2	1.28	138.3	27.7	17.4
C ₄ mim[SCN]	197.3	1.07	156.9	28.9	22.3
C ₂ mim[CH ₃ CO ₂]	170.3	1.10	128.0	28.5	20.4
C ₄ mim[CH ₃ CO ₂]	198.3	1.06	136.0	26.7	13.8

[a] From <https://iolitec.de/>. [b] From ref. ^[21]. [c] Calculated according to Eq. 8. [d] Calculated according to Eq. 9. [e] From Table S3. [f] From Table 3. [g] From Table 1.

Table 5. Calculations of solubility parameter χ_{21} of Cs[NTf₂] and Li[NTf₂] in imidazolium based ionic liquids.

IL	MW/ g · mol ⁻¹	$\rho_{293K}^{(a)}$ g · cm ⁻³	$\Delta_1^g H_m^\circ$ (298.15 K) ^(b) kJ · mol ⁻¹	χ_{21} / ^(c) Cs[NTf ₂]	χ_{21} / ^(c) Li[NTf ₂]
C ₂ mim[NTf ₂]	391.3	1.52	127.7	4.8	6.1
C ₄ mim[NTf ₂]	419.4	1.44	134.9	6.7	8.3
C ₆ mim[NTf ₂]	447.4	1.37	140.1	9.2	11.1
C ₄ mim[PF ₆]	284.2	1.37	146.5	0.5	0.9
C ₄ mim[SCN]	197.3	1.07	156.9	0.1	0.1

[a] From <https://iolitec.de/>. [b] From ref. ^[21]. [c] Calculated according to Eq. 9.

3. Conclusions

Vaporization thermodynamics of the ionic liquids [Ph₄P][NTf₂] and Cs[NTf₂] was studied with the help of the QCM method. Experimental vaporization enthalpies were adjusted to the reference temperature 298.15 K. Solubilities of ionic compounds in practically relevant solvents were assessed.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: ionic liquids · solubility · thermal stability · vaporization enthalpy · vapor pressure

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