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Vaporisation Thermodynamics: Are Triazolium Ionic Liquids a Real Alternative to Popular Imidazolium-Based Ionic Liquids?

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Abstract: New experimental vapour pressures and vaporisation enthalpies of the *ionic liquids* [2,4-dimethyl-1,2,4-triazolium][NTf$_2$], [2-methyl-4-ethyl-1,2,4-triazolium][NTf$_2$], and [2-ethyl-4-methyl-1,2,4-triazolium][NTf$_2$] were measured using the Langmuir method in combination with the quartz crystal microbalance. New experimental vapour pressures and vaporisation enthalpies of the *molecular liquids* 1H-1,2,4-triazole, 1-methyl-1,2,4-triazole, 1-ethyl-1,2,4-triazole, and 1H-1,2,3-triazole were measured using the transpiration method. Structure–property relationships between molecular and ionic liquids were studied. These results will facilitate chemical engineering calculations of processes involving ILs.

Keywords: ionic liquid; vapour pressure; enthalpy of vaporisation; structure–property relationships

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1. Introduction

Triazolium-based ionic liquids (ILs) are considered a new class of solvents for cellulose. The cations of these ILs are structurally similar to the popular imidazolium cations, but the 1,2,4- and 1,2,3-triazolium cations lack the isolated ring proton, which leads to a lower formation of N-heterocyclic carbenes and thus to a lower reactivity and fewer undesired side reactions [1–3]. Triazolium ILs can be easily produced in high purity and without contamination by halides, can be a good alternative to "classical" imidazolium ILs for a number of applications, and can even enable new applications [4].

Since the ILs are generally regarded as neoteric solvents, the solution to practical questions concerning miscibility, separation of mixtures, volatilisation, vapour pressure, thermal stability, etc., requires knowledge of thermodynamic data. Such data are not yet available for the new triazolium ILs. This work extends our previous studies on ILs containing fluorinated anions [5–8] and deals with the vaporisation thermodynamics of 1,2,4-triazolium-based ILs with the [NTf$_2$] anion (see Figure 1).

The experimental data on the vapour pressures and vaporisation enthalpies of the three ionic liquids [di-a1kyl-1,2,4-triazolium][NTf$_2$] provide only limited information on the thermal properties of this new class of solvents. It is therefore important to compare these new data with those for "classical" imidazolium-based ILs in order to qualitatively assess the advantages and disadvantages of the new materials. In this context, we will refer to our previous results on the vaporisation thermodynamics of the [C$_n$mim][NTf$_2$] family [5] for comparison.

In fact, the experimental investigation of the vapour pressures of extremely low volatile ILs is a very challenging task, which is why a sufficient amount of thermal data for triazolium-based ILs can hardly be expected in the near future. For this reason, the development of reliable methods for predicting vaporisation thermodynamics could be important for chemical engineering calculations. The experience gained in our recent studies through a systematic comparison of "*molecular* liquids versus *ionic* liquids" [9–11] could be used in this work to predict the vaporisation enthalpies of 1,2,4-triazolium and 1,2,3-triazolium ILs paired with the [NTf_2] anion. For this purpose, the vapour pressures of the *molecular liquids* (triazoles) shown in Figure 2 were measured, and their vaporisation enthalpies were involved in structure–property correlations with the corresponding triazolium-based *ionic liquids*.

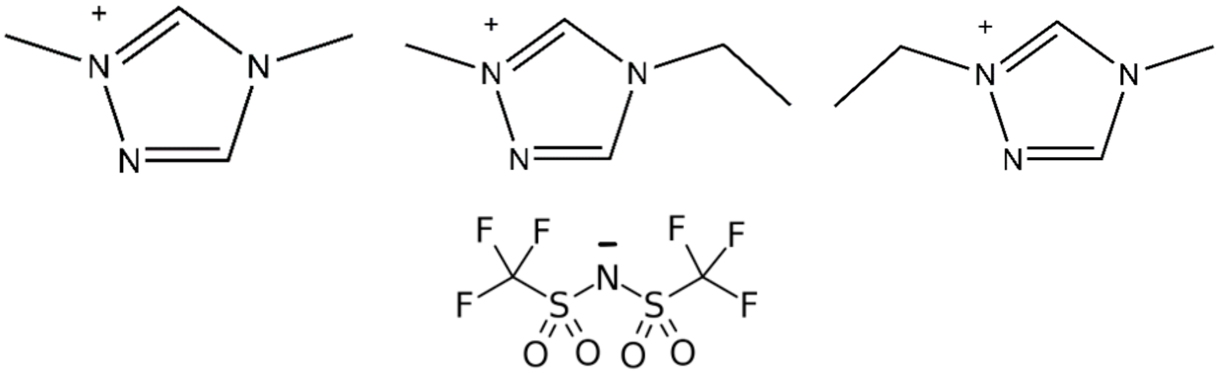

Figure 1. *Ionic liquids* under study in this work: [2,4-dimethyl-1,2,4-triazolium][NTf_2], [2-methyl-4-ethyl-1,2,4-triazolium][NTf_2], and [2-ethyl-4-methyl-1,2,4-triazolium][NTf_2], with the anion [NTf_2] = (trifluoromethylsulfonyl)imide. The abbreviations [2-C_n-4-C_m-1,2,4-T][NTf_2] with n, m = 1, 2 are helpful for the presentation of the data in the tables in this paper.

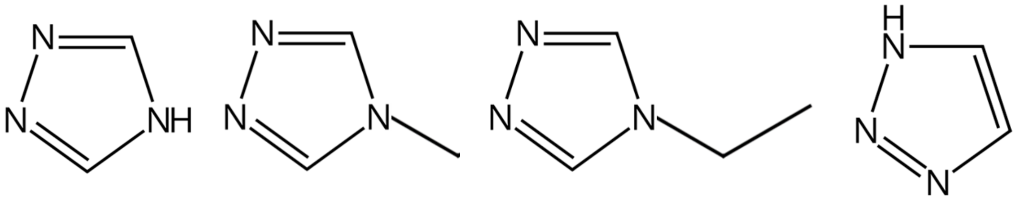

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Figure 2. *Molecular liquids* under study in this work: 1H-1,2,4-triazole, 1-methyl-1,2,4-triazole, 1-ethyl-1,2,4-triazole, and 1H-1,2,3-triazole.

2. Experimental Section

2.1. Materials

The *ionic liquid* samples [2,4-dimethyl-1,2,4-triazolium][NTf_2], [2-methyl-4-ethyl-1,2,4-triazolium][NTf_2], and [2-ethyl-4-methyl-1,2,4-triazolium][NTf_2] used in this work were prepared and purified by Dr. hab. Andrzej Skrzypczak, Poznań University of Technology, Institute of Chemical Technology and Engineering, Poznań, Poland, who passed away in 2023. The degree of purity of >99% was determined using the HPLC method.

Prior to the experiments, the samples were vacuum-evaporated for more than 24 h at 413 K and 10^{-5} Pa to reduce possible traces of solvents and moisture. The samples used for the vaporisation studies using a quartz crystal microbalance (QCM) were additionally conditioned within 12 h in the vacuum chamber at the highest temperature of the experiment. This additional purification allowed the removal of residual traces of water and volatile impurities as well as the collection of a sufficient amount of vaporised IL on the quartz sensor required for FTIR analysis.

The *molecular liquid* samples 1H-1,2,4-triazole, 1-methyl-1,2,4-triazole, 1-ethyl-1,2,4-triazole, and 1H-1,2,3-triazole were of commercial origin. Provenance and purities are listed in Table S1 (Supplemental Materials). Before starting the vapour pressure measurements with the transpiration method, the samples were preconditioned in the saturator (see below for details). The purity of samples was analysed with a Hewlett Packard 5890 II series gas chromatograph equipped with a flame ionisation detector and an HP-5 capillary column (length, inside diameter, and film thickness of 25 m × 0.32 mm × 0.25 µm). The GC temperature programme started at T = 323 K, followed by heating at a rate of 0.167 $K \cdot s^{-1}$ to T = 573 K.

2.2. Absolute Vapour Pressure Measurements

The vapour pressures and standard molar enthalpies of vaporisation of the ILs were determined using the QCM method [5,12]. In this method, a sample of an IL is placed in an open measuring cavity within the thermostat block and exposed to a vacuum (10^{-5} Pa) with the entire open surface (Langmuir evaporation). The sensor is located directly above the cavity containing the sample. During evaporation in a vacuum, a certain amount of the sample is deposited on the quartz crystal. The change in the vibrational frequency of the crystal is directly related to the mass of the compound deposited on the crystal in a given time. The molar standard enthalpies of vaporisation were derived from the temperature dependencies of the experimentally measured change in the vibration frequency of the quartz crystal. The essential experimental details are provided in the Supplemental Materials.

The vapour pressures and standard molar enthalpies of vaporisation of the molecular liquids (1H-1,2,4-triazole, 1-methyl-1,2,4-triazole, 1-ethyl-1,2,4-triazole, and 1H-1,2,3-triazole) were determined using the transpiration method [13]. In this method, a stream of nitrogen was passed through the saturator filled with the sample at a precisely defined flow rate at a constant temperature (±0.1 K). After reaching saturation equilibrium in the saturator, the material transported by the gas flow was collected in a cold trap within a defined time and its mass was determined by GC. The standard molar enthalpies and entropies of vaporisation were derived from the temperature dependence of the absolute vapour pressures. The necessary details can be found in the Supplemental Materials.

3. Results and Discussion

3.1. Absolute Vapour Pressures and Vaporisation Thermodynamics of Ionic Liquids

Admittedly, one of the most important attributes of ionic liquids is that they have a negligible vapour pressure (compared to the common molecular solvents). However, this statement applies more to ambient temperatures, and it is obvious that at higher temperatures, which are relevant for chemical engineering, the vapour pressure already assumes a considerable size and should be quantified for the development of future technologies. For example, reliable knowledge of the temperature dependence of the vapour pressure of ILs is essential for the optimisation of modern catalytic processes such as Solid Catalyst with Ionic Liquid Layer (SCILL) [14] or Supported Ionic Liquid Phase (SILP) [15] in order to assess a possible long-term uptake of ILs at any practical temperature. The experimental vapour pressures at different temperatures for the triazolium ILs measured in this work are collected in Table S2. The equations used to approximate the experimental data allow the vapour pressure to be calculated at any practically relevant temperature. The 373 K and 473 K temperatures appear to be reasonable choices for many practical applications, and the extremely low values of [NTf_2]-based IL vapour pressures at these temperatures (see Table 1) indicate that the negligible mass uptake of IL in various catalytic or separation applications can also be expected at elevated temperatures.

Table 1. Absolute vapour pressures of ILs [2-C_n-4-C_m-1,2,4-T][NTf_2] with n, m = 1, 2 at 373 K and at 473 K.

Cation	$p_{sat} \times 10^6$ [Pa]	$p_{sat} \times 10^3$ [Pa]
	373 K	473 K
[2-C_1-4-C_1-1,2,4-T]	20	70.8
[2-C_1-4-C_2-1,2,4-T]	36	134.8
[2-C_2-4-C_1-1,2,4-T]	35	121.5

The absolute vapour pressure data of ILs are still rarely available in the literature, and it is interesting to compare the general vapour pressure values within the families of imidazolium-based ILs with fluorinated anions $[CF_3SO_3]^-$, $[PF_6]^-$, $[BF_4]^-$, and $[NTF_2]^-$ (see Figure 3).

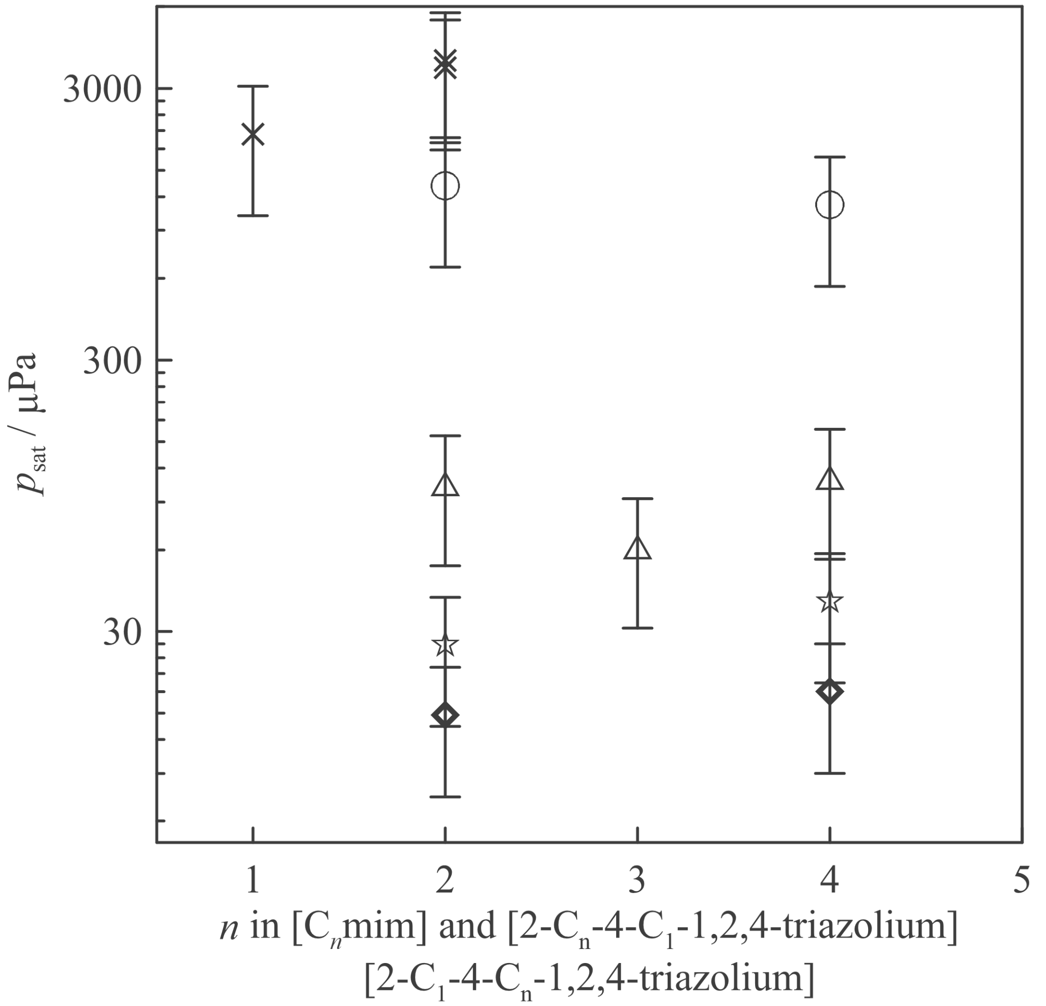

Figure 3. Vapour pressures of typical ILs. Chain-length dependence of absolute vapour pressures at T = 423.15 K for homologous series: (Δ)—[$C_n$mim][CF_3SO_3] from [16], (○)—[$C_n$mim][NTf_2] [5], (◊)—[$C_n$mim][PF_6] from [7], (☆)—[$C_n$mim][BF_4] from [6], and (x)—[2-C_n-4-C_m-1,2,4-triazolium][NTf_2] from this work.

Figure 3 shows that the vapour pressures of [di-alkyl-1,2,4-triazolium][NTf_2] are several times higher than those of ILs based on the [BF_4] and [PF_6] anions. The values of the absolute vapour pressures of the [di-alkyl-1,2,4-triazolium][NTf_2] and [$C_n$mim][NTf_2] series do not differ significantly. The apparent decrease in vapour pressure for ILs with the [C_2mim] cation compared to ILs with the [C_4mim] cation appears to be common for this series of ILs with [PF_6] and [BF_4] anions and is not as pronounced for ILs with the same cation but [NTf_2] and [CF_3SO_3] anions. In the case of [di-alkyl-1,2,4-triazolium][NTf_2], replacing one of the CH_3 substituents with C_2H_5 leads to an almost twofold increase in vapour pressure. Such an increase can be interpreted as an even–odd effect in the vaporisation properties for ILs with a short alkyl chain. A similar dependence is observed for [$C_n$mim][CF_3SO_3] when going from n = 3 to 4 [16].

The standard molar enthalpies of vaporisation of ionic liquids (see Table 2) were derived from the temperature dependence of the absolute vapour pressures given in Table S2 (see for details in Supplemental Materials).

Table 2. Thermodynamics of vaporisation of [2-C_n-4-C_m-1,2,4-T][NTf_2] with n, m = 1, 2 derived from experimental results [a].

IL Triazole Cation	T-Range	T_{av}	$\Delta_l^g H_m^o(T_{av})$ [b]	$\Delta_l^g G_m^o(T_{av})$ [c]	$\Delta_l^g C_{p,m}^o$ [d]	$\Delta_l^g H_m^o$(298 K) [e]
	K		kJ·mol^{-1}		J·K^{-1}·mol^{-1}	kJ·mol^{-1}
1	2	3	4	5	6	7
[2-C_1-4-C_1-1,2,4-T]	348-395	371.0	122.2 ± 1.0	69.5 ± 1.0	−49	125.7 ± 1.2
[2-C_1-4-C_2-1,2,4-T]	345-393	368.4	123.7 ± 1.0	68.1 ± 1.0	−57	127.7 ± 1.3
[2-C_2-4-C_1-1,2,4-T]	343-390	365.9	122.4 ± 1.0	68.5 ± 1.0	−57	126.3 ± 1.3

[a] Uncertainties of thermodynamic functions are expressed as the standard uncertainty. [b] The standard molar enthalpy of vaporisation at the average temperature, T_{av}, of the QCM experiment. [c] The standard Gibbs energies of vaporisation at the average temperature, T_{av}, of the QCM experiment. [d] From Table S3. [e] Adjusted to 298 K according to Kirchhoff's Law using the $\Delta_l^g C_{p,m}^o$–values from column 6. The experimental QCM uncertainties were extended with uncertainty of the heat capacity difference assessed to be of 20 J·K^{-1}·mol^{-1}.

The vaporisation enthalpies of triazolium-based ionic liquids were determined for the first time. However, it is interesting to compare these results with those known for imidazolium-based ionic liquids that are paired with the same [NTf_2] anion and have a comparable number of C atoms in the alkyl chains attached to the cation. It has been found that the $\Delta_l^g H_m^o$(298 K) = 122.7 ± 1.1 kJ·mol^{-1} [5] of [C_1mim][NTf_2] is slightly lower than that of [2-C_1-4-C_1-1,2,4-T][NTf_2] from this work. The vaporisation enthalpy $\Delta_l^g H_m^o$(298 K) = 126.4 ± 1.1 kJ·mol^{-1} [5] of [C_2mim][NTf_2] is almost the same as that of the corresponding triazolium-based ILs [2-C_1-4-C_2-1,2,4-T][NTf_2] and [2-C_2-4-C_1-1,2,4-T][NTf_2] (see Table 2). In general, however, the results for the triazolium- and imidazolium-based ILs can be considered to agree within their combined uncertainties. This similarity opens up the possibility of establishing structure–property correlations between the imidazolium-based ILs (for which a considerable amount of vaporisation thermodynamics data are available) and the triazolium-based ILs, whose data are only limited by the results of the current study. This correlation will be discussed in Section 3.4.

3.2. Absolute Vapour Pressures and Vaporisation Thermodynamics of Molecular Liquids: 1,2,4-Triazoles

The primary vapour pressure–temperature dependencies for 1H-1,2,4-triazole, 1-methyl-1,2,4-triazole, 1-ethyl-1,2,4-triazole, and 1H-1,2,3-triazole measured in this work (see Table S4) were fitted uniformly using a three-parametric equation (see Supplemental Materials for details). From these data, the standard molar enthalpies of vaporisation/sublimation at the respective temperatures T were derived (see Table S4). The final results at the reference temperature T = 298 K, $\Delta_{l,cr}^g H_m^o$(298 K), are summarised and compared in Table 3.

As can be seen from Table 3, the available experimental data for 1H-1,2,4-triazole are confusing. Our complementary transpiration measurements for this compound have helped to resolve inconsistencies and determine the level of enthalpy of sublimation for this compound. The weighted average $\Delta_{cr}^g H_m^o$(298 K) = 84.3 ± 0.5 kJ·mol^{-1} was recommended for thermochemical calculations. The latter value was combined with the fusion enthalpy for this compound (see Table S5) to derive the vaporisation enthalpy $\Delta_l^g H_m^o$(298 K) = 71.2 ± 1.0 kJ·mol^{-1} of 1H-1,2,4-triazole (see Table 3), which is essential as "*molecular liquid*" for the purpose of this work. The vapour pressures and vaporisation enthalpies for 1-methyl-1,2,4-triazole, 1-ethyl-1,2,4-triazole, and 1H-1,2,3-triazole were measured for the first time in this work.

Table 3. Compilation of available enthalpies of sublimation/vaporisation $\Delta_{cr,l}^{g}H_{m}^{o}$ for triazoles.

Compound/CAS	M [a]	*T*-Range	$\Delta_{cr,l}^{g}H_{m}^{o}(T_{av})$	$\Delta_{cr,l}^{g}H_{m}^{o}$(298 K) [b]	Ref.
		K	kJ·mol^{-1}	kJ·mol^{-1}	
1H-1,2,4-triazole (cr)	K	322–350	84.1 ± 1.0	84.6 ± 1.0	[17]
	n/a			(80.6 ± 0.5)	[18]
	K	281.5–295.7	84.1 ± 1.3	84.0 ± 1.3	[19]
	C	306.0	80.5 ± 0.9	(80.6 ± 0.9)	[20]
	T	322.2–367.5	83.7 ± 0.6	84.3 ± 0.7	Table S4
				84.3 ± 0.5 [c]	average
1H-1,2,4-triazole (liq)				71.2 ± 1.0	Table S5
1-methyl-1,2,4-triazole (liq)	T	275.0–337.8	53.1 ± 0.3	53.4 ± 0.4	Table S4
1-ethyl-1,2,4-triazole (liq)	T	280.6–313.1	57.0 ± 0.4	56.8 ± 0.5	Table S4
1H-1,2,3-triazole (liq)	T	297.2–348.7	59.9 ± 0.4	59.9 ± 0.4	Table S4
1-methyl-1,2,3-triazole (liq)				44.0 ± 1.5	Figure 4
1-ethyl-1,2,3-triazole (liq)				47.0 ± 1.5	Figure 5

[a] Techniques: K = Knudsen-effusion method; T = transpiration method; C = calorimetry; n/a = not available. [b] Uncertainty of the sublimation/vaporisation enthalpy $U(\Delta_{cr,l}^{g}H_{m}^{o})$ is the expanded uncertainty (0.95 level of confidence, k = 2) calculated according to a procedure described elsewhere [21,22]. It includes uncertainties from the experimental conditions, uncertainties of vapour pressure, uncertainties from the fitting equation, and uncertainties from temperature adjustment to *T* = 298 K. [c] Weighted mean value (the uncertainties were used as a weighting factor). Values in parentheses were excluded from the calculation of the mean. Value in bold is recommended for further thermochemical calculations.

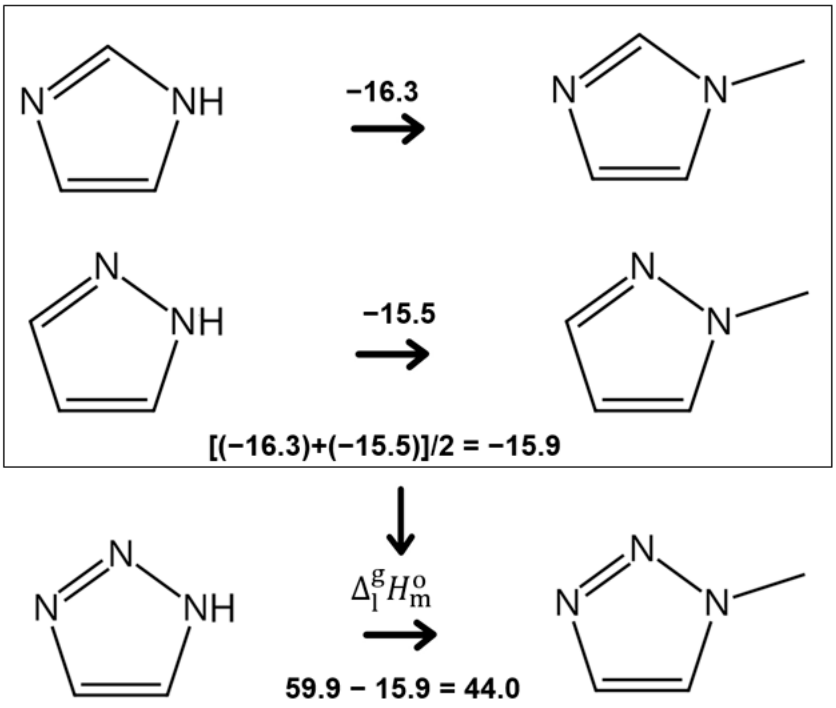

Figure 4. Evaluation of the vaporisation enthalpy, $\Delta_{l}^{g}H_{m}^{o}$(298 K), for 1-methyl-1,2,3-triazole using structure–property relationships. Experimental data are listed in Table 3 and Table S6. (All data are given in kJ·mol^{-1}).

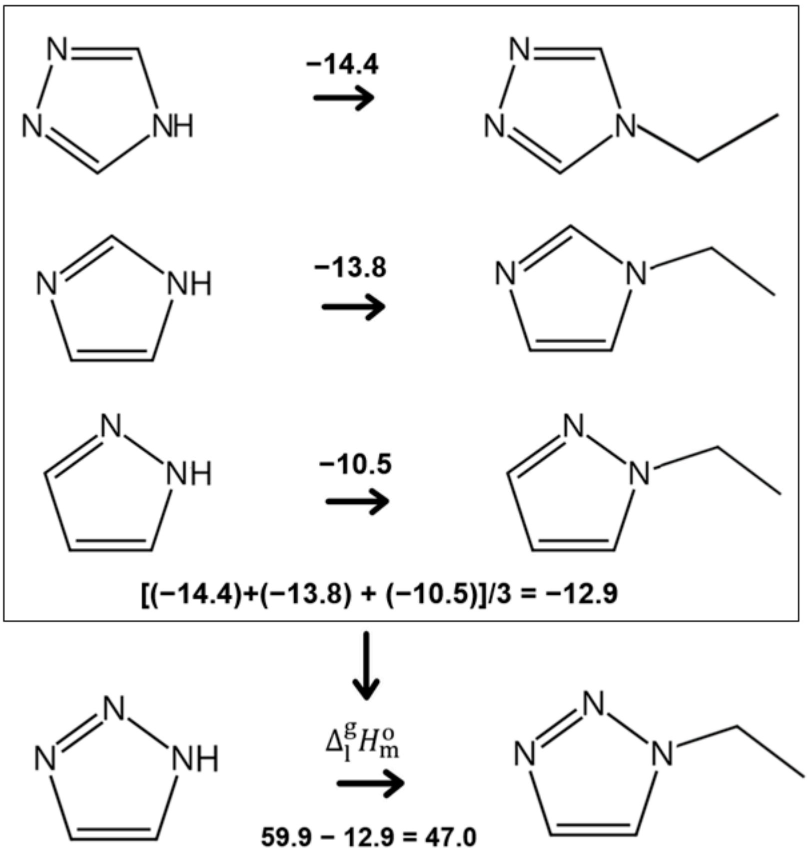

Figure 5. Evaluation of the vaporisation enthalpy, $\Delta_l^g H_m^o$(298 K), for 1-ethyl-1,2,3-triazole using structure–property relationships. Experimental data are listed in Table 3 and Table S6. (All data are given in kJ·mol^{-1}).

3.3. Vaporisation Thermodynamics of Molecular Liquids: 1,2,3-Triazoles

From the 1,2,3-triazole family, only 1H-1,2,3-triazole was commercially available for thermodynamic studies. For the purposes of this work, the vaporisation enthalpies for 1-methyl-1,2,3-triazole and 1-ethyl-1,2,3-triazole are required for the structure–property correlations with the corresponding ionic liquids. To assess these vaporisation enthalpies, we used reliable thermodynamic data on imidazole and alkylimidazoles as well as on pyrazole and alkylpyrazoles from the literature (see Table S6). The idea of evaluation is shown in Figure 4.

It has turned out that the replacement of the hydrogen bonded to the nitrogen atom in both 1-H-imidazole and 1H-pyrazole by the CH_3 group lowers the vaporisation enthalpies for both molecules by ≈16 kJ·mol^{-1} (see Figure 4). It can therefore be assumed that the same decrease can also be expected for 1H-1,2,3-triazole. With the known vaporisation enthalpy $\Delta_l^g H_m^o$(298 K) = 59.9 ± 0.4 kJ·mol^{-1} of 1H-1,2,3-triazole (see Table 3) and the averaged contribution H → CH_3 = −15.9 kJ·mol^{-1} (see Figure 4), the required vaporisation enthalpy $\Delta_l^g H_m^o$(298 K) = 44.0 ± 1.5 kJ·mol^{-1} of 1-methyl-1,2,3-triazole was derived (see Table 3).

A similar idea was realised for 1-methyl-1,2,3-triazole, where the averaged contribution H → CH_3CH_2 = −12.9 kJ·mol^{-1} (see Figure 5) was added to $\Delta_l^g H_m^o$(298 K) = 59.9 ± 0.4 kJ·mol^{-1} of 1H-1,2,3-triazole (see Table 3) to obtain the required vaporisation enthalpy $\Delta_l^g H_m^o$(298 K) = 47.0 ± 1.5 kJ·mol^{-1} of 1-ethyl-1,2,3-triazole (see Table 3).

3.4. Molecular versus Ionic Liquids: Structure–Property Relationships for Predicting Vaporisation Thermodynamics

It is noticeable that the vaporisation enthalpies of heterocycles with two or three nitrogen atoms have very similar vaporisation enthalpies (see Figure 6).

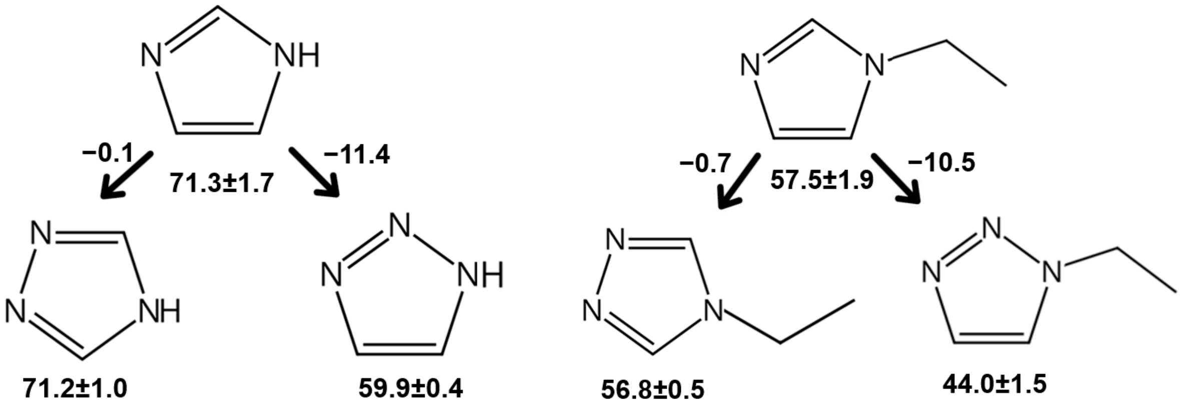

Figure 6. Comparison of the vaporisation enthalpies, $\Delta_l^g H_m^o$(298 K), of 1-H-imidazole with those of 1H-1,2,4-triazole and 1H-1,2,3-triazole (**left**). Comparison of the vaporisation enthalpies, $\Delta_l^g H_m^o$(298 K), of 1-ethyl-imidazole with those of 1-ethyl-1,2,4-triazole and 1-ethyl-1,2,3-triazole (**right**). Experimental data are from Table 3 and Table S6. (All data are given in kJ·mol^{-1}).

Indeed, $\Delta_l^g H_m^o$(298 K) = 71.2 ± 1.0 kJ·mol^{-1} of 1H-1,2,4-triazole (see Table 3) is indistinguishable from $\Delta_l^g H_m^o$(298 K) = 71.3 ± 1.7 kJ·mol^{-1} of 1H-imidazole (see Table S6). Also, $\Delta_l^g H_m^o$(298 K) = 56.8 ± 0.5 kJ·mol^{-1} of 1-ethyl-1,2,4-triazole (see Table 3) is almost the same as the $\Delta_l^g H_m^o$(298 K) = 57.5 ± 1.9 kJ·mol^{-1} of 1-ethyl-imidazole (see Table S6). A similar trend was already observed in Section 3.1 for the triazolium- and imidazolium-based ILs.

As a matter of fact, the vaporisation thermodynamics of the [C$_n$mim][NTf$_2$] *ionic liquids* family with alkyl chain length n = 1 to 18 are well established [5], and the reliable vaporisation enthalpies, $\Delta_l^g H_m^o$(298 K), are compiled in Table S7. The reliable vaporisation enthalpies, $\Delta_l^g H_m^o$(298 K), of the corresponding *molecular liquids* of the 1-alkyl-imidazole family with alkyl chain length n = 1 to 18 are also known and are summarised in Table S7. The correlation of the $\Delta_l^g H_m^o$(298 K)-values of molecular liquids (axis X) and ionic liquids (axis Y) is shown in Figure 7.

As can be seen from this plot, there is a remarkable linear correlation between the $\Delta_l^g H_m^o$(298 K)-values for the [C$_n$mim][NTf$_2$] family and the 1-alkyl-imidazole family:

$$\Delta_l^g H_m^o([\mathrm{C_n mim}][\mathrm{NTf_2}]) = 0.9781 \times \Delta_l^g H_m^o(\text{1-alkyl-imidazole}) + 69.1 \text{ with } R^2 = 0.9989$$

The very high correlation coefficient R^2 can be seen as proof of the good consistency of the experimental data for each family.

It is now interesting to know how the 1,2,4-triazolium-based ILs are associated with this correlation. The experimental vaporisation enthalpies for these *ionic liquids* from Table 2 and their corresponding *molecular liquids*, 1-methyl-1,2,4-triazole and 1-ethyl-1,2,4-triazole from Table 3, are plotted in Figure 7, and the points are highlighted in red. Figure 7 shows that the point for [2-C$_1$-4-C$_1$-1,2,4-T][NTf$_2$] is slightly above the line, but this outlier is to be expected since such behaviour of the first representatives in the homologous series is typical for *ionic* and *molecular* liquids [5]. However, the points for [2-C$_1$-4-C$_2$-1,2,4-T][NTf$_2$] and [2-C$_2$-4-C$_1$-1,2,4-T][NTf$_2$] lie practically (within the uncertainties) on the correlation of the imidazole derivatives. This observation suggests that the vaporisation enthalpies of ILs based on 1,2,4-triazolium with a longer than ethyl chain length are likely to be very similar to those of the corresponding [C$_n$mim][NTf$_2$] family. This assumption is important for chemical engineering calculations with the alkyl-1,2,4-triazolium-based ILs, which are promising for various practical applications [23].

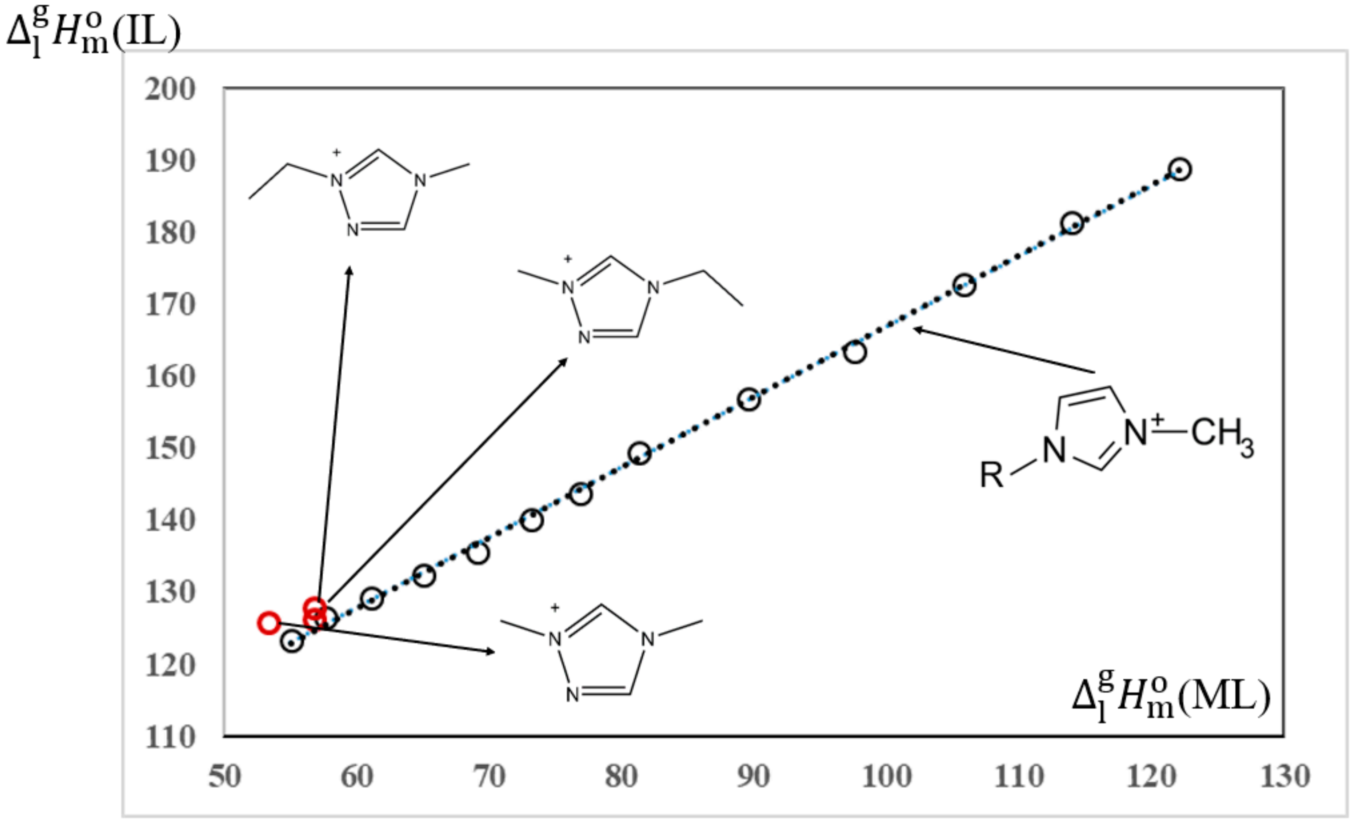

Figure 7. The correlation of the $\Delta_l^g H_m^o$(298 K)-values of *molecular liquids* (axis *X*) versus *ionic liquids* (axis *Y*). Experimental data are listed in Table 3, Tables S6 and S7. (All data are given in kJ·mol^{-1}).

What about the vaporisation enthalpies, $\Delta_l^g H_m^o$(298 K), of the 1,2,3-triazolium-based ILs which are even more promising than 1,2,4-triazolium-based ILs [24,25]? To approach the answer to this question, we compare the experimental data for heterocycles in Figure 6. While the derivatives of 1-H-imidazole and 1-H-1,2,4-triazole have very close $\Delta_l^g H_m^o$(298 K)-values, the derivatives of 1-H-1,2,3-triazole, in contrast, are obviously and systematically more volatile by ≈11 kJ·mol^{-1}. These systematics, in conjunction with the structure–property observations specific to imidazolium and triazolium ILs evident in Figure 7, suggest that the vaporisation enthalpies for the [alkyl-1,2,3-triazolium][NTf_2] family could be reliably estimated from the data for the [$C_n$mim][NTf_2] family by subtracting 11 kJ·mol^{-1} from imidazolium-based ILs of the corresponding chain length. These estimates can be reliably used for chemical engineering calculations with the alkyl-1,2,3-triazolium-based ILs required for various practical applications.

4. Conclusions

Structure–property correlations between similarly shaped *ionic* and *molecular* liquids have proven to be a valuable tool to determine the consistency of experimental data within homologous series and to reveal general trends in vaporisation thermodynamics. These trends allow an assessment of the vaporisation enthalpies, $\Delta_l^g H_m^o$(298 K), of new ILs with the help of the well-established data for imidazolium-based *ionic liquids* combined with the evaluated data for *molecular liquids*.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/liquids4030032/s1, Table S1: Provenance and purity of ILs studied in this work. Table S2: Details on vapor pressure measurements with Quartz-Crystal Microbalance. Results for vapor pressure temperature dependence and vaporization enthalpies determined by QCM. Table S3: Details on vapour pressure measurements of molecular liquids using the transpiration method. Compilation of data on molar heat capacities heat capacity differences. Table S4: Results of transpiration method: absolute vapour pressures, standard molar vaporisation/sublimation enthalpies and standard molar vaporisation/sublimation entropies. Table S5: Thermodynamics of phase transitions of 1H-1,2,4-triazole. Table S6: Auxiliary data for vaporisation enthalpies of nitrogen containing heterocycles available from the literature. Table S7: Compilation of enthalpies of vaporization for [Cnmim][NTf2] and for alkyl-imidazole. Figure S1: The scheme of the QCM experimental setup. Figures S2–S4: The IR spectra for ionic liquids under study. Figure S5: The scheme of the transpiration experimental setup. References [5,7,12,13,21,22,26–37] are cited in the Supplementary Materials.

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