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Review

Imidazolium Based Ionic Liquids: Unbiased Recovering of Vaporization Enthalpies from Infinite-Dilution Activity Coefficients

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Abstract: We propose and test an efficient approach for the assessment of the enthalpies of vaporization of ionic liquids at the reference temperature 298.15 K. The approach is based on activity coefficients at infinite dilution of volatile organic solutes in ionic liquids bearing the imidazolium cation of the general formula $[C_n mim][Anion]$.

1. Introduction

In the last two decades, ionic liquids (ILs) have been considered as potential solvents to replace volatile organic solvents in chemical technologies, as they possess negligible vapour pressure and they cannot evaporate (even at elevated temperatures) and cause air pollution. Typical protic ILs are comprised of a quaternary cation (imidazolium, ammonium, phosphonium, and pyridinium, etc.) with a wide variety of common anions. Their physical and thermodynamic properties can be deliberately tuned by the choice of the cation, anion, and substituents implemented into the cation or anion structure. To develop ILs for the various practical applications, it is important to gain a fundamental knowledge of the factors that control the volatility and thermal stability of pure ILs, as well as the phase behaviour of ionic liquids with other common solvents and chemicals. Since 2001, our laboratory has contributed to this fundamental understanding and prediction of IL properties. We have launched our work with the development of the gas-chromatographic method for determination of infinite-dilution activity coefficients [1]. Activity coefficients at infinite dilution of a solute γ_1^∞ in ionic liquid are important for the optimal design of separation processes. They are especially important when the last traces of impurities must be removed. Knowledge on activity coefficients helps to avoid an oversizing of distillation columns or stripping processes. Moreover, γ_1^∞ values provide information about the intermolecular interactions between solvent and solute; in particular, they are used for the selection of solvents for extraction and extractive distillation.

From the very beginning of the ILs era, there were two crucial advantages propagated for ILs: negligible vapour pressure and inflammability. Both predications have been challenging for our thermochemical lab specialised on vapor pressure measurements and combustion calorimetry. Thus, the long-standing concept of ILs involatility has been disproved with our first quantitative measurements on ILs vapor pressure [2]. Additionally, the acknowledged postulate of ILs inflammability has been disproved by our very first combustion energy measurements of 1-butyl-3-methylimidazolium dicyanamide [3]. Furthermore, we suggested the combination of calorimetric methods (combustion calorimetry and differential scanning calorimetry [4]) with quantum-chemical and molecular dynamic calculations for the "indirect" appraisal of ILs vaporization enthalpies [5]. At the same time,

we have intensively developed "direct" experimental methods for ILs vapor pressures and vaporization enthalpy measurements. The main challenges for this method are that, at ambient temperatures, the extremely low vapor pressures of ILs are practically negligible and difficult to measure, whereas, at elevated temperatures, the vaporization process is very often aggravated by the thermal degradation. Nevertheless, we optimized experimental conditions of the conventional transpiration method for the reliable determination of the ILs' vapor pressures temperature dependences [3,5]. Moreover, we demonstrated that the thermogravimetric analysis (TGA) can be successfully used not only for the common thermal stability studies, but also for the reliable vaporization enthalpy determinations at elevated temperatures [6]. Indeed, it was found that thermal stability of many ILs was not always sufficient to exclude decomposition in the temperature range of the TGA study. In order to overcome the limitations due to the thermal instability of the ILs, we have developed an extremely sensitive quartz-crystal microbalance (QCM) method to determine the ILs' vapor pressures [7]. The enormous sensitivity of the quartz-crystal (placed over a cavity filled with IL) for the detection of a minute amount of ionic liquid, vaporised and deposited on the surface, has allowed a drastic drop in experimental temperatures (e.g., a starting temperature of the QCM-study of 353 K!) feasible for reliable determination of the mass loss and elimination of thermal decomposition as a consequence. Confronting the ever-questionable thermal stability of ILs at elevated temperatures, we have also invented a method for determining ILs' volatility at the nanoscale by means of ultra-fast scanning calorimetry (UFSC) [8]. The idea behind this method is to reduce the residence time of the IL sample at all experimental temperatures. It can be achieved by extremely high heating and cooling rates (up to 10^5 K s^{-1}) of the sample placed on the sensor developed for the heat capacity measurements. Thus, the residence time of the IL at high temperature required for measurable mass uptake was optimised to some minima. One consequence was that the chemical processes of thermal degradation hardly have time to begin, as the sample is quickly cooled to ambient temperature. With the UFSC method (based on extremely high heating/cooling rates), much higher experimental temperatures (as compared to common techniques) can be reached without significant decomposition. For example, it was demonstrated that evaporation of 1-ethyl-3-methylimidazolium bis(trifluoromethyl-sulfonyl)imide ([C$_2$mim][NTf$_2$]) at temperatures of up to 750 K is still the dominating process of mass loss, even at such highly elevated temperatures [8]. Despite the success of the suppression of decomposition during the TGA, QCM, and UFSC measurements, the idea of decreasing the temperatures of IL studies seems to be more attractive and practically relevant. Complementary to the development of the low-temperature QCM-method, we have come up with an idea to use alternating current chip calorimetry (AC) for vapor pressure measurements of ILs at low temperatures [9]. A small droplet of an IL is vaporized isothermally from the chip sensor in a vacuum chamber. The highly sensitive chip sensor (SiN$_x$-membrane) allows for mass loss determination at temperatures also starting from 350 K. Finally, it is worth mentioning that the data set on vapor pressures, created for [C$_2$mim][NTf$_2$] from experiments with AC and UFSC methods for the extremely broad temperature range from 358 K to 780 K, has allowed the estimation of the boiling temperature of this IL. The value (1120 ± 50) K should be considered as the first reliable boiling point of the archetypical ionic liquid obtained from experimental vapor pressures measured in the closest possible proximity to the normal boiling temperature [9].

The systematic development and mutual validation of experimental methods for vapor pressure and vaporisation enthalpies, $\Delta_l^g H_m^o$, of the extremely low-volatile ionic liquids delineated above, have been a focus of our scientific interests for the past two decades. As a result, consistent sets of experimental vapor pressures and vaporization enthalpies for imidazolium- [1–13], pyridinium- [14–17], pyrrolidinium- [17,18], and phosphonium- [19] based ionic liquids have been reported in the current literature. There is a broad demand for these data, as they are essential for the effective utilization of ILs such as thermofluids, or in separation processes, where precise thermodynamic data on solvents and working fluids are required. Absolute vapor pressures of ILs are indispensable for their modern

catalytic applications such as Solid Catalysts with Ionic Liquid Layer (SCILL) [20] or a supported ionic liquid phase (SILP) [21]. The vital question in both cases is: is the IL vapor pressure in the catalytic temperature range low enough in order to avoid the uptake from the catalyst layer? The correct answer is important for the large-scale applications of the generally expensive ionic liquids.

Apart from the practical importance, vaporization enthalpy is one of the key values required for parameterization and optimization of the ILs' force field for molecular dynamics simulations [22]. Moreover, the systematic information on vaporization energetics within well-defined ionic liquid families opens the way for fundamental understanding of the structure–property relationships in ILs, essential for a reliable prediction of their thermodynamic properties [23]. The latter values are crucial for the optimisation of IL synthesis reactions [24] or IL use for the synthesis of nanoparticles [25].

Admittedly, all standard thermodynamic properties used in practical thermochemical calculations are referenced to any common temperature (most frequently T = 298.15 K). As is apparent from the survey of the experimental method for vaporization enthalpy determination outlined above, none of these methods provide the $\Delta_l^g H_m^o$(298.15 K) values. As a rule, the measured vaporization enthalpies are referenced to the average temperature T_{av} of the experimental interval. These $\Delta_l^g H_m^o(T_{av})$ values have to be adjusted to the reference temperature T = 298.15 K according to the Kirchhoff's Rule [2,3,10] by using appropriate $\Delta_l^g C_{p,m}^o$ values. Formally, the value $\Delta_l^g C_{p,m}^o = C_{p,m}^o(g) - C_{p,m}^o(l)$ is the difference of the molar heat capacities of the gaseous $C_{p,m}^o(g)$ and the liquid phase $C_{p,m}^o(l)$, respectively. However, the ambiguity and prospects of the $\Delta_l^g C_{p,m}^o$ values required for the adjustment of experimental vaporization enthalpies $\Delta_l^g H_m^o(T_{av})$ to the reference temperature T = 298.15 K have already been discussed in detail [10]. Nevertheless, any new idea for independent assessment of $\Delta_l^g H_m^o$(298.15 K) values is valuable and desired.

Fortunately, in a series of our recent IL studies [26–28] we have been able to show that the $\Delta_l^g H_m^o$(298.15 K) values can be derived from the collection of activity coefficients at infinite dilution γ_1^∞ of a solute *1*, in an ionic liquid (solvent *2*) measured by using gas–liquid chromatography (GLC). These studies [26–28] were performed on imidazolium based ILs with the trifluoroacetate [CF_3CO_3], trifluoromethanesulfonate [CF_3SO_3], and methanesulfonate [CH_3SO_3] anions. Is this observation also generally valid for imidazolium based ILs containing other types of anions? If yes, the method based on the experimental γ_1^∞ values can be suggested as an independent source for the $\Delta_l^g H_m^o$(298.15 K) values, as well as for the valuable validation of $\Delta_l^g C_{p,m}^o$ values applied for the temperature adjustment of experimental $\Delta_l^g H_m^o(T_{av})$ values. Our pioneering paper on GLC determination of activity coefficients of aliphatic and aromatic compounds in 4-methyl-*N*-butyl-pyridinium tetrafluoroborate [1] has inspired the ionic liquid community. Indeed, according to the most recent compilation [29], a comprehensive experimental data base covering 233 ILs and 150 molecular solutes was extracted from 182 references, dealing with activity coefficients at infinite dilution. This huge data pool could be considered as an independent source for the $\Delta_l^g H_m^o$(298.15 K) values for numerous differently structured ILs, provided that the procedure for the recovery of vaporisation enthalpies from solute γ_1^∞ values is successful. In order to keep this task in size, in this study we selected only imidazolium-based ILs where the $\Delta_l^g H_m^o$(298.15 K) values were measured and evaluated in our recent papers.

2. Experimental Background

Activity coefficient at infinite dilution γ_1^∞ of a solute (index 1) in an ionic liquid (index 2) is a valuable thermodynamic tool for the interpretation of intermolecular interactions between a solvent (ILs in this work) and a solute (any volatile compound in this work). Experimental measurements are performed with a commercial gas-chromatograph (GC) equipped with a flame-ionization or a thermal conductivity detector. The ionic liquid (solvent) is used as a stationary phase coating the solid support (diatomaceous earths) in a packed column. Small amounts of organic solutes (0.5 to 2 μL) are injected into the GC

column. The retention times are recorded and corrected for the "dead time" (retention time of air or methane).

According to the fundamental work by Cruickshank et al. [30], the retention time is generally proportional to the standardized retention volume V_N:

$$ln\gamma_1^\infty = ln\left(\frac{n_{IL} \cdot R \cdot T}{V_N \cdot p_1^0}\right) - \frac{B_{11} - V_1^0}{RT} \cdot p_1^0 + \frac{2 \cdot B_{13} - V_1^\infty}{RT} \cdot J_{GC} \cdot p_0 \tag{1}$$

where p_1^0 is the vapour pressure of the pure liquid solute and n_{IL} is the number of moles of the stationary phase component (ionic liquid) on the column. The factor J_{GC} corrects for the influence of the pressure drop along the column. The second and third term in Equation (1) are correction terms which arise from the non-ideality of the mobile gaseous phase. B_{11} is the second virial coefficient of the solute, B_{13} is the mixed virial coefficient of the solute (1) with the carrier gas nitrogen (index 3), V_1^0 is the liquid molar volume of pure solute, and V_1^∞ is the partial molar volume of solute in the ionic liquid at infinite dilution (with assumption $V_1^\infty = V_1^0$). Molar volumes of solutes V_1^0 are estimated using experimental densities. The values of B_{11} and B_{13} are estimated according to the Tsonopolous method [31]. A detailed description of the experimental procedure can be found elsewhere [1,30,32]. Values of γ_1^∞ are claimed to be accurate within $\pm (3 \div 5)$ %. The γ_1^∞ values are usually measured at temperatures not too distant from the reference temperature $T = 298.15$ K and they are practically not affected by the temperature adjustment. For this reason, the γ_1^∞-based estimations of $\Delta_l^g H_m^o$(298.15 K) are especially valuable, as they can prove different approaches applied for the temperature adjustments of the vaporization enthalpies from the T_{av} to 298.15 K.

3. Theoretical Background

In this work we follow the Flory–Huggins theory, which is the main basis of solution and blend thermodynamics [33]. The Flory–Huggins equation handles molecules that are similar chemically, but differ greatly in size. A key value of this theory is a parameter χ_{12} quantifying the enthalpic interactions between the components *1* and *2*. The activity coefficient at infinite dilution γ_1^∞ is linked to the Flory−Huggins interaction parameter χ_{12} (at infinite dilution) according to the equation [34]:

$$\chi_{12} = \ln\left(\frac{273.15 \; \gamma_1^\infty M_2}{T M_1}\right) - \left(1 - \frac{V_1^*}{V_2^*}\right) + \ln\left(\frac{\rho_1}{\rho_2}\right) \tag{2}$$

where M_1 and M_2 are the molecular weight of solute and solvent, respectively, and V_1^* and V_2^* and ρ_1 and ρ_2 are the molar volume and density of solute and solvent, respectively. The Flory–Huggins interaction parameters, χ_{12} is related to the Hildebrandt solubility parameters δ [34]:

$$\chi_{12} = \frac{V_1^*(\delta_1 - \delta_2)^2}{RT} \tag{3}$$

where δ_2 is the solubility parameter of the IL (solvent) and δ_1 is the solubility parameter of the solute, R is the universal gas constant, T is the arbitrary temperature, and V_1^* is the molar volume of the solute at the selected temperature. Solubility parameters are the numerical values that are responsible for the strength of the intermolecular interactions between solute and solvent molecules. The solubility parameters have been widely used as they help to assess the solvation powers of solvents.

The Hildebrand or total solubility parameter (δ_i) is defined as follows [35]:

$$\delta_i = \left[\left(\Delta_l^g H_m^o - RT\right)/V_m\right]^{0.5} \tag{4}$$

where V_m is the molar volume, $\Delta_l^g H_m^o$ is the standard molar enthalpy of vaporization, R is the ideal gas constant, and T is the temperature. Vaporization enthalpies, $\Delta_l^g H_m^o$, of ionic

liquids required for calculations δ_2 at $T = 298.15$ K have been systematically evaluated in our recent work. Vaporization enthalpies, $\Delta_l^g H_m^o$, of molecular solutes required for calculations δ_1 at $T = 298.15$ K were taken from the literature [36,37]. Values of the solubility parameters δ_1 and δ_2 have been calculated according to Equation (4) with help of experimental data on vaporization enthalpies for the solutes [36]. Density values for the solutes were taken from the compilation by Lide [37], and for ILs from the NIST Database [38].

Finally, the algebraic rearrangement of Equation (3) gives:

$$\frac{\delta_1^2}{RT} - \frac{\chi_{12}}{V_1^*} = \left(\frac{2\delta_2}{RT}\right)\delta_1 - \frac{\delta_2^2}{RT} \tag{5}$$

As it was shown in a typical case (see Figure 1), when the left side of Equation (5) is plotted against δ_1, then the mathematical term $2\delta_2/(RT)$ is the slope of the line and the module $-\delta_2^2/(RT)$ is its intercept. Using linear regression of the experimental data, the slope or intercept can be used to determine δ_2.
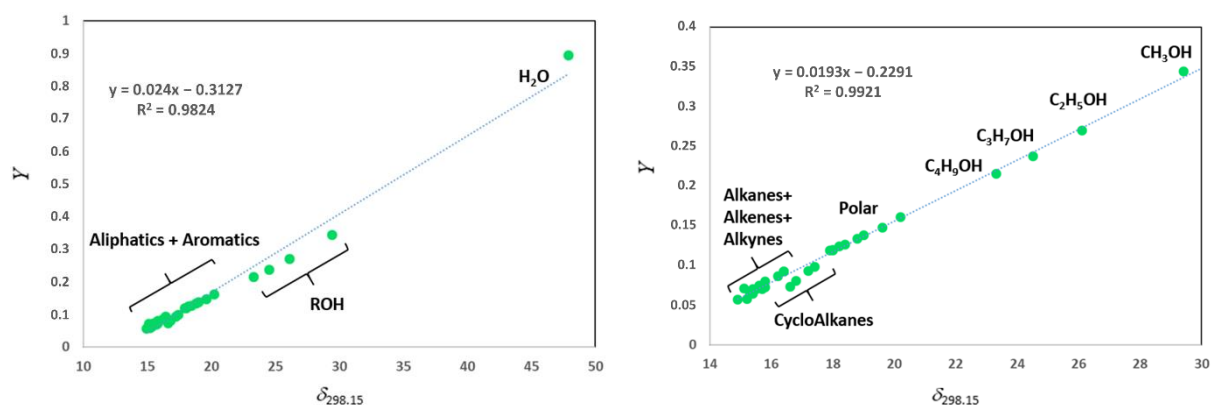
Figure 1. Regression of solubility parameters $\delta_{298.15}$ of different solutes and Y-module ($Y = (\delta_1)^2/(RT) - \chi_{12}/V_1^*$ is the left part of Equation (5)) for [C$_6$mim][SCN] derived from experimental γ_1^∞ values [39]. (**Left**): the whole data. (**Right**): the same data set, but with the experimental point for water removed.

We fitted Equation (5) with the solubility parameters δ_2 derived from primary γ_1^∞ values for the [C$_n$mim][Anion] available in the literature. For each data set, the solubility parameters δ_2 obtained using the slope and intercept were in agreement with one another within 3%. Thus, the δ_2 values can be estimated as the average from the slope and the intercept. Thus, the vaporization enthalpy, $\Delta_l^g H_m^o(298.15$ K), of an IL under study was calculated using the averaged δ_2 value as follows:

$$\Delta_l^g H_m^o(T) = \left[\delta_2^2 \times V_m + RT\right] \tag{6}$$

where all values, including V_m, are referenced to an arbitrary temperature T, which is 298.15 K in this work. Now these $\Delta_l^g H_m^o(298.15$ K) results, "indirectly" derived with help of the primary γ_1^∞-values, can be used for comparison with the "direct" experimental results on vaporization enthalpies obtained by the conventional methods.

4. Inspection of Activity Coefficients γ_1^∞ Placed at the Disposal

Experimental γ_1^∞ values for different solutes in different types of ILs are regularly appearing in the literature, beginning in 2001 with the aprotic ionic liquids [1] and, ten years later, the protic ionic liquids [40,41]. As a rule, the set of γ_1^∞ values reported for a particular ionic liquid consists of $15 \div 40$ solutes of different polarity. In the majority of cases, solutes are subdivided into groups: *n*-alkanes with the chain-length C$_5$–C$_{10}$, cycloalkanes with the chain-length C$_5$–C$_8$, alkenes with the chain-length C$_5$–C$_8$, alkynes with the chain-length C$_5$–C$_8$, benzene and alkylbenzenes with the chain-length C$_1$–C$_3$, and linear and

branched aliphatic alcohols with the chain-length C_1–C_5, as well as a number of solutes of different polarity: acetone, acetonitrile, thiophene, tetrahydrofuran, aliphatic ethers, and esters. In addition, the water is also included if the studies are performed with the thermal conductivity detector. A typical example of the regression of solubility parameters $\delta_{298.15}$ derived from the experimental γ_1^∞ values is given in Figure 1. For demonstration, we have deliberately chosen the data set containing water (see Figure 1Left). It is apparent that the solubility parameter of water due to the exceedingly high polarity is totally out of correlation with all other types of solutes. Therefore, it is senseless to keep this molecule in the set for regression of solubility parameters. The same data set but without water looks more appropriate (see Figure 1Right), but in this iteration it is obvious that subsets of linear and cyclic aliphatics (alkanes, alkenes, and alkynes) definitely demonstrate individual behavior, and the $\delta_{298.15}$ points represent a cloud rather than a decent linear attitude. It is noticeable that the cyclical molecules deviate even more drastically from the general trend. We could suggest at least two possible reasons for the variations observed. The first reason is an objective one—the individual behavior of alkane, alkene, and alkyne series can be considered as evidence of specific intermolecular interactions between the different types of aliphatics and the IL under study. Compounds with the double or triple bond are expected to interact with the polar framework of the IL more intensively than the similarly shaped alkanes. Additionally, the cyclic molecules interact with the IL differently than linear molecules, containing the same number of C-atoms. This explanation is in accordance with the general thermodynamic interpretation of the γ_1^∞ values, which are meaningful for interpretation of intermolecular interactions between solutes and solvents.

The second reason for the significant spread of the $\delta_{298.15}$ points on Figure 1 is a rather subjective one. From our own experiences, the γ_1^∞ measurements are thwarted with considerable technical complications. The main troubles are due to the very short retention times of the highly volatile aliphatics. Even at the low temperatures of the GC experiment, and by using the long packed columns, the retention times of the C_5–C_7 hydrocarbons are close to the "dead time", and the γ_1^∞ values can be significantly affected by the inaccuracy of the time registration. Moreover, in the GC experiment, the C_5–C_7 hydrocarbons usually eluate in the immediate vicinity after the solvent peak (e.g., CH_2Cl_2). Admittedly, the tail of the solvent peak still contains sufficient residual amounts of solvent molecules dissolved in the IL layer covering the solid support. The solute of interest (one of C_5–C_7 hydrocarbons) not only interacts with the IL, but also with the residual CH_2Cl_2 molecules and, as a consequence, the true retention time is counterfeit. Thus, the unavoidable solvent peak tailing also contributes to the inaccuracy of the time registration. The practical conclusion for the further γ_1^∞ values acquisition is that the experimental points for C_5–C_6 hydrocarbons (alkanes, alkenes, and alkynes) should be omitted.

In contrast to the very volatile C_5–C_6 hydrocarbons, the retention times measured for a series of different polar compounds (e.g., acetone, benzene, alkylbenzenes, and ethers) are not affected by the experimental perturbations. Additionally, a reasonable correlation of solubility parameters $\delta_{298.15}$ of different solutes with the *Y*-module has been virtually observed (see Figure 2Left). However, such a good correlation is rather due to the fact that the series of polar compounds involved in the examination belongs to a relatively narrow range of $0.1 \div 0.3$ units, according to the normalized solvent polarity scale [42]. For this reason, the moderate intensity of intermolecular interactions between each solute with the IL-solvent is localized at a comparable level, reflecting the individual straight line for the polar compounds in Figure 2Left.
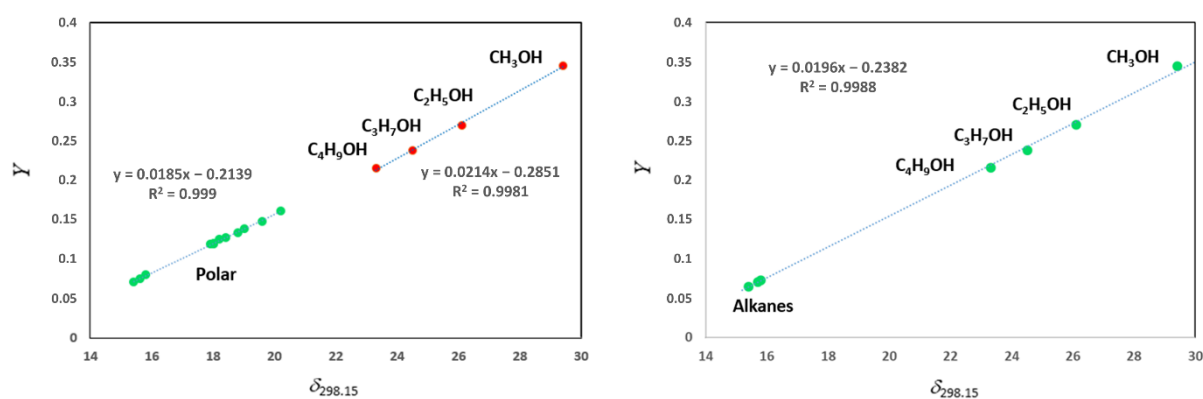
Figure 2. Regression of solubility parameters $\delta_{298.15}$ of different solutes and Y-module ($Y = (\delta_1)^2/(RT) - \chi_{12}/V_1^*$ is the left part of Equation (5)) for [C$_6$mim][SCN] derived from experimental γ_1^∞ values [39]. (**Left**): separate treatment of collection of polar molecules (see text) and aliphatic alcohols. (**Right**): joint treatment of linear alkanes and linear alcohols.

The energetics of interactions of alcohol molecules with the IL is expected to be more profound, as their polarities range from 0.75 (methanol) to 0.60 (1-propanol) in units of the normalized solvent polarity scale [42]. Subsequently, the ROH series (methanol, ethanol, 1-propanol, and 1-butanol) also represents the individual straight line (see Figure 2Left).

5. Development of Activity Coefficients γ_1^∞ Data Acquisition and Processing

We have deliberately launched the discussion of the γ_1^∞ measurements with the most consistent data set reported for the for [C$_6$mim][SCN] [39]. However, among the available literature compilations on the γ_1^∞ values for imidazolium based ILs of the general formula [C$_n$mim][Anion], we have dealt with many less consistent data sets. For example, the γ_1^∞ values for series including benzene and alkylbenzenes, alcohols (1-propanol, 2-propanol, and 2-methyl-1-propanol), polar solutes (acetone, acetonitrile, ethyl acetate, 1,4-dioxane, and tetrahydrofuran), and halogen containing solutes (dichloromethane, trichloromethane, 1,2-dichloromethane, chlorobenzene, and bromobenzene) were reported for [C$_6$mim][CF$_3$CO$_2$] [43].

The regression of solubility parameters $\delta_{298.15}$ of different solutes with the Y-module for [C$_6$mim][CF$_3$CO$_2$] is presented in Figure 3. Numerical values used for this correlation are collected in Table S2. The significant spread of the experimental data points is apparent on Figure 3, especially for the polar compounds such as acetone, acetonitrile, 1,4-dioxane, and trichloromethane. Most probably, this scatter is an indication of more pronounced intermolecular interactions between these solutes with the [C$_6$mim][CF$_3$CO$_2$] in comparison to [C$_6$mim][SCN]. Certainly, one or the other outlier can be cancelled in order to minimize scattering. However, each removed point inevitably leads step by step to the significant change of the slope and intercept of the regression presented on Figure 3. As a consequence, the δ_2-result (and finally the $\Delta_l^g H_m^o$(298.15 K)-result, calculated according to Equation (6)) becomes questionable and virtually dependant on manipulations with the data set on γ_1^∞ values. Moreover, the resulting $\Delta_l^g H_m^o$(298.15 K) value for the IL under study becomes crucially dependent on the collection of γ_1^∞ values selected for the evaluation. This conclusion is easy to support with numerical results obtained from Figure 2, right. The value $\Delta_l^g H_m^o$(298.15 K) = 115.1 kJ·mol^{-1} is calculated using the selection of "polar" solutes. The value $\Delta_l^g H_m^o$(298.15 K) = 152.8 kJ·mol^{-1} is calculated using only the set of alcohols. Seemingly, such a significant disagreement leaves no hope for practical application of γ_1^∞ values for the $\Delta_l^g H_m^o$(298.15 K) appraisal. Nevertheless, let us recall and rationalise the background of the disagreement once more. In general, each available γ_1^∞ data set comprises a series of non-polar solutes (e.g., *n*-alkanes), weakly polar solutes (e.g., alkylbenzenes, ethers, and esters, etc.), and strongly polar solutes (usually alcohols). Each subset exhibits specific intensity of intermolecular interactions with the IL-solvent. Apparently, the slopes of the δ_1(298.15 K)–Y regressions (see Figures 1–3) constructed for

each subset of γ_1^∞-values could be helpful to quantify the specific energetics of these forces. Unfortunately, the scales of the δ_1(298.15 K) values and Y values for non-polar and weakly polar solutes are impractically narrow. For example, the variations of δ_1(298.15 K) values for aliphatics are only from 15.2 to 17.4 MPa$^{0.5}$ (see Table S1), and the variations for Y values for the same series are from 0.0583 to 0.0989 unities (see Table S1) [26]. As a rule, slopes derived in restricted ranges of parameters are very sensitive and suffer from the individual uncertainties of experimental data points. The variation of δ_1(298.15 K) values and Y values for series of weakly polar solutes is somewhat broader (see Table S1), but still insufficient for establishment of robust correlations. Additionally, only the scale of δ_1(298.15 K) values and Y values for alcohols ROH with R = methyl, ethyl, *n*-propyl, and *n*-butyl (see Table S1 and Figure 1Right) is adequate for the reliable regression (e.g., the variations of δ_1(298.15 K) values is from 29.4 to 23.3 MPa$^{0.5}$, as well as the variations for Y values is from 0.3450 to 0.2155 unities (see Table S1) [26]. It is only regrettable in that papers where at least four C$_1$–C$_4$ alcohols are measured are quite restricted, precluding any meaningful interpretation of results for this series.
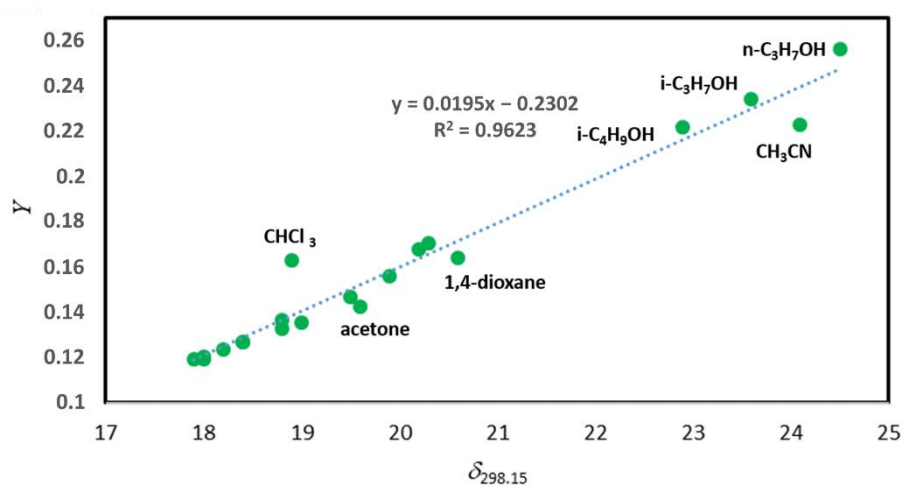
Figure 3. Regression of solubility parameters $\delta_{298.15}$ of different solutes and Y-module ($Y = (\delta_1)^2/(RT) - \chi_{12}/V_1^*$ is the left part of Equation (5)) for [C$_6$mim][CF$_3$CO$_2$] derived from experimental γ_1^∞ values [43].

The temporary conclusion for the continuation and development of γ_1^∞ values evaluation is that the none of individual subsets of solutes can be used for a reliable assessment of vaporisation enthalpies $\Delta_l^g H_m^o$(298.15 K). However, what speaks against combination of two subsets (see Figure 2Right)? Indeed, by the merging the *n*-alkanes subset with the alcohol subset, we are capturing both edge cases: explicitly weak intermolecular interactions and explicitly strong intermolecular interactions. This idea facilitates an insight into the relationships between activity coefficients γ_1^∞ of solutes in solvent (IL) and vaporisation enthalpy $\Delta_l^g H_m^o$(298.15 K) of the solvent (IL). It is the basic knowledge, that activity coefficient γ_1^∞ is the measure for strength of interactions between solute and solvent. Additionally, the vaporization enthalpy is the measure of intermolecular forces in pure solvent. Capturing the γ_1^∞ values only for the edge cases (*n*-alkanes + alcohols), we establish an unbiased average level of intermolecular energetics, which is fixed to the well-defined, restricted set of solutes. Provided that this set will be common for any ionic liquid, the regression of γ_1^∞ values (see Figure 2Right) becomes an unbiased thermodynamic tool for recovering vaporisation enthalpy $\Delta_l^g H_m^o$(298.15 K). Such a strict limitation only to the set (*n*-alkanes + alcohols), allows crucial simplification of the γ_1^∞ values evaluation, as the regression δ_1(298.15 K)–Y is represented now by practically impeccable straight line (see Figure 2Right). Merging the *n*-alkanes and alcohols subsets is felicitous from the mathematical point of view, as the best possible scales of δ_1(298.15 K) values (from 15.2 to

29.4 MPa$^{0.5}$) and of *Y* values (from 0.0583 to 0.3450 unities) are now encompassed for the γ_1^∞ values evaluation (see Figure 2Right). What is more, the conscious acquisition of only *n*-alkanes and alcohol subsets releases oneself from the troublesome analysis of δ_1(298.15 K)–*Y* regressions (see Figures 1–3) and the desperate retrieval of outliers justification. For the sake of brevity, the procedure of γ_1^∞ values evaluation with help of merged alkanes and alcohols subsets along this paper is designate as "heptane–methanol" or *HM* approach (as both solutes are most frequently present in the published data sets and they configure the frame of data acquisition). In our opinion the *HM* approach could be considered as the virtually unbiased tool for examination of γ_1^∞ and $\Delta_l^g H_m^o$(298.15 K) interrelations.

6. Examination of the *HM* Approach

For a preliminary validation of the *HM* approach it is senseless to examine all 184 available papers [29] on γ_1^∞ values. Imidazolium based ionic liquids have been the most intensively studied in the current literature, and it is reasonable to test *HM* approach with data on the [C$_n$mim][Anion] series. Among them, the most popular series of ILs was that associated with the NTf$_2$-anion. Enthalpies of vaporisation $\Delta_l^g H_m^o$(298.15 K) for this series of ionic liquids have been published recently [10]. They were used for the reconciliation with results derived from γ_1^∞ values reported in the literature [44–55]. Most of the data were measured by the GLC technique. Some data sets were also measured by the dilutor technique, but results from both methods have been shown to be indistinguishable. For the sake of transparency, we have preferred the comprehensive studies of activity coefficients, and we have omitted some papers dealing only with separating industrially relevant binary systems (e.g., hexane/hexane, etc.). The γ_1^∞ values available in the literature at temperatures other than *T* = 298.15 K have been adjusted to this reference temperature by using the linear extrapolation $\ln(\gamma_1^\infty) = f\ (1/T)$. We fitted Equation (5) with the solubility parameters δ_2 derived from primary γ_1^∞ values with help of Equations (2)–(4) for the [C$_n$mim][Anion] available in the literature, and estimated the $\Delta_l^g H_m^o$(298.15 K) values according to Equation (6). Typical results of the data treatment for the [C$_n$mim][NTf$_2$] series are given in Table 1.

Table 1. [C$_n$mim][NTf$_2$] series: comparison of $\Delta_l^g H_m^o$ (298.15 K) values derived according to Equations (5) and (6) with experimental results from conventional methods.

IL	$\Delta_l^g H_m^o$(exp) [a]	$\Delta_l^g H_m^o$(GLC) [b]	$\Delta_l^g H_m^o$(HM) [c]	F$_{im}$ [d]	Ref. [e]
[C$_2$mim][NTf$_2$]	127.7 ± 1.8 [10]	119.0	125.3	1.02	[49]
		115.3	125.5	1.02	[50]
		133.3	134.1	0.95	[51]
[C$_4$mim][NTf$_2$]	134.9 ± 1.7 [10]	129.2	134.3	1.00	[52]
			132.7	1.02	[53]
[C$_6$mim][NTf$_2$]	139.9 ± 1.8 [10]	133.9	138.5	1.01	[45]
		131.4	140.3	1.00	[46]
		143.5	144.4	0.97	[47]
			141.1 [f]	0.99	[45,48]
[C$_8$mim][NTf$_2$]	147.1 ± 2.0 [10]	145.8	148.4	0.99	[46]
[C$_{10}$mim][NTf$_2$]	154.6 ± 2.5 [10]	151.1	155.0	1.00	[54]
[C$_{12}$mim][NTf$_2$]	161.5 ± 1.8 [10]		161.1	1.00	[55]
				1.00 ± 0.01	

[a] Experimental values derived from different conventional techniques and evaluated and reported in our recent papers. [b] Estimated according to Equations (5) and (6) using γ_1^∞ values for all solutes reported in original papers. [c] Estimated according to Equations (5) and (6) using γ_1^∞ values for only *n*-alkanes and alcohols reported in original papers. [d] Correction factor F$_{im}$ = $\Delta_l^g H_m^o$(exp)/$\Delta_l^g H_m^o$(HM). [e] References for the experimental γ_1^∞ values. [f] Combination of γ_1^∞ data set of alcohols [48] with the γ_1^∞ data set for *n*-alkanes [45].

Experimental vaporization enthalpies are listed in column 2. In the first iteration, we processed all γ_1^∞ values presented in the particular paper. The single data point for water was removed from regression, but all other outliers remained at this step. Vaporisation enthalpies calculated in this way are given in column 3. Without going too deeply into the details and peculiarities of each data set, as well as in reason of agreement or disagreement for each individual IL from Table 1, it is quite apparent that the blind application of the traditional δ_1(298.15 K)–Y regression is guesswork. Of course, the quality of each individual experimental data point is definitely responsible for the final quality of correlation. However, explicitly for the [C$_6$mim][NTf$_2$], the special IUPAC project [44] was designed for testing different methods of γ_1^∞ values. According to the final IUPAC conclusions for the majority of measurements where different techniques were used, the agreement is generally within the expected uncertainties for the measurement methods [44]. However, this optimistic conclusion is not able to explain the dramatic scattering of $\Delta_l^g H_m^o$(298.15 K) values from 131.4 to 154.0 kJ·mol^{-1} calculated for the [C$_6$mim][NTf$_2$] (see Table 1, column 3). It is worth mentioning that four contributors [45–48] of γ_1^∞ values listed for this IL in Table 1 were participants of this IUPAC project. Additionally, what about the *HM* approach? Results derived from this approach are given in Table 1, column 4. Let us examine the *HM* approach applied to [C$_6$mim][NTf$_2$] data sets, where the γ_1^∞-values are seemingly of certified and impeccable quality. The most comprehensive γ_1^∞-data set was reported by Heintz et al. [45] and it comprised twelve alcohols (from methanol to *n*-hexanol, iso-propyl-, iso-butyl-, sec-butyl-, tert-butyl-, and tert-pentyl-alcohols) and six *n*-alkanes (from *n*-heptane to *n*-dodecane).

The value $\Delta_l^g H_m^o$(298.15 K) = 138.5 kJ·mol^{-1} for [C$_6$mim][NTf$_2$] derived from the γ_1^∞ data set by Heintz et al. [45] is in very good agreement with the experimental value 139.9 ± 1.8 (see Table 1, column 2). The less extensive collection of γ_1^∞ values was reported by Kato and Gmehling [46]. It included only methanol, ethanol, *n*-propanol, iso-propanol, and only two *n*-alkanes (*n*-heptane and *n*-octane). The value $\Delta_l^g H_m^o$(298.15 K) = 140.3 kJ·mol^{-1} for [C$_6$mim][NTf$_2$] derived from their γ_1^∞ data set is also in perfect agreement with the experimental value (see Table 1, column 2). The modest γ_1^∞ data set was reported by Letcher et al. [47] and it consisted from methanol, *n*-heptane, and *n*-octane. The value $\Delta_l^g H_m^o$(298.15 K) = 144.4 kJ·mol^{-1} for [C$_6$mim][NTf$_2$] derived from this very limited γ_1^∞ data set is in acceptable agreement with the experimental value (see Table 1, column 2). The γ_1^∞ data set reported by Dobryakov et al. [48] consists only of eight linear and branched alcohols, thus the data treatment according to the *HP* approach is not possible. However, we could combine the alcohols set from Dobryakov et al. [48] with the reliable *n*-alkanes set from Heintz et al. [45] and the joined treatment of these γ_1^∞ data provides the value $\Delta_l^g H_m^o$(298.15 K) = 141.1 kJ·mol^{-1} for [C$_6$mim][NTf$_2$], which agrees well with the experiment. Summing up the experiences with the *HM* approach application towards [C$_6$mim][NTf$_2$] data, it is obvious, that the "traditional" treatment (see Table 1, column 3) of the whole set of γ_1^∞ values measured for the non-polar and polar solvent is not able to reproduce the reliable vaporization enthalpies measured by conventional methods (see Table 1, column 2). In contrast, the application of the *HM* approach allows estimated values that can be compared well with the experiment. This conclusion is supported by the comparison of the "theoretical" $\Delta_l^g H_m^o$(298.15 K) values derived from the *HM* approach for the [C$_n$mim][NTf$_2$] series with n = 2, 4, 6, 8, 10, and 12 (see Table 1), as well as for the [C$_n$mim][CF$_3$CO$_2$] series with n = 2 and 6 (see Table 2).

Table 2. [$C_n$mim][CF_3CO_2] series: comparison of $\Delta_l^g H_m^o$ (298.15 K) values derived according to Equations (5) and (6) with experimental results from conventional methods [a].

IL	$\Delta_l^g H_m^o$(exp)	$\Delta_l^g H_m^o$(GLC)	$\Delta_l^g H_m^o$(HM)	F_{im}	Ref.
[C_2mim][CF_3CO_2]	126.4 ± 1.5 [26]	122.3	126.4	1.00	[56]
[C_6mim][CF_3CO_2]	141.5 ± 1.9 [26]	183.2	143.8	0.98	[43]
				0.99 ± 0.01	

[a] The definition of symbols is the same as in Table 1.

Such a good correspondence between "theoretical" and experimental $\Delta_l^g H_m^o$(298.15 K) values has motivated further systematic comparisons. The results for [$C_n$mim][Anion] series with [CF_3SO_3], [CH_3SO_3], and [Cl] anions are collected in Table 3.

Table 3. [$C_n$mim][Anion] series with [CF_3SO_3], [CH_3SO_3], and [Cl]: comparison of $\Delta_l^g H_m^o$ (298.15 K) values derived according to Equations (5) and (6) with experimental results from conventional methods [a].

IL	$\Delta_l^g H_m^o$(exp)	$\Delta_l^g H_m^o$(GLC)	$\Delta_l^g H_m^o$(HM)	F_{im}	Ref.
[C_2mim][CF_3SO_3]	134.2 ± 2.5 [27]	108.0	110.1	1.22	[57]
[C_4mim][CF_3SO_3]	138.7 ± 2.4 [27]	116.7 [b]	120.6	1.15	[58,59]
		121.2	123.9	1.12	[60]
[C_6mim][CF_3SO_3]	146.1 ± 2.4 [27]	137.6 [c]			[61]
				1.16 ± 0.03	
[C_2mim][CH_3SO_3]	141.4 ± 1.9 [28]	120.5	120.0	1.18	[62]
		111.8	121.0	1.17	[63]
		122.7	123.1	1.15	[64]
[C_4mim][CH_3SO_3]	149.8 ± 2.1 [28]	126.5	136.6	1.10	[65]
				1.15 ± 0.02	
[C_4mim][Cl]	153.3 ± 1.9 [66]	140.5	138.3	1.11	[65]
[C_6mim][Cl]	160.5 ± 2.4 [66]	132.2	135.0	1.19	[67]
[C_8mim][Cl]	166.8 ± 3.8 [66]		154.9	1.08	[65]
				1.13 ± 0.03	

[a] The definition of symbols is the same as in Table 1. [b] Combination of γ_1^∞ data set of *n*-alkanes [58] with the γ_1^∞ data set for alcohols [59]. [c] Estimated from data set containing γ_1^∞ values only for alkylbenzenes and low polar solutes.

To our surprise, column 2 and column 4 of Table 3 reveal that the "theoretical" values are systematically underestimated in comparison to the "experimental" values. In an attempt to be strict and stringent, we have determined a factor $F_{im} = \Delta_l^g H_m^o(\text{exp})/\Delta_l^g H_m^o(HM)$ (see Tables 1–3, 5 and 6 and Section 6 column 5) in order to quantify the degree of underestimation. We found that for the IL series collected in Table 3, the factor F_{im} is close to unity (1.13 to 1.16) for each type of the IL. Additionally, it is important that F_{im} is hardly dependent on the chain-length within each series.

For the development of the *HP* approach it is essential to trace whether the factor F_{im} is accidental, or if it is possibly anion-specific for each [$C_n$mim][Anion] series. In Table **??**, we evaluated results of regressions for the [$C_n$mim][Anion] series with fluorine-containing anions [BF_4], [PF_6], and [FAP].

Table 4. $[C_n mim][Anion]$ series with fluorine-containing anions: comparison of $\Delta_l^g H_m^o$ (298.15 K) values derived according to Equations (5) and (6) with experimental results from conventional methods [a].

IL	$\Delta_l^g H_m^o$(exp)	$\Delta_l^g H_m^o$(GLC)	$\Delta_l^g H_m^o$(HM)	F_{im}	Ref.
$[C_2 mim][BF_4]$	130.5 ± 2.9 [16]	101.1	103.2	1.26	[68]
		95.3	104.1	1.25 [b]	[69]
$[C_4 mim][BF_4]$	138.3 ± 2.7 [16]	106.5	108.1	1.28	[70]
		105.0	108.5	1.27	[71]
		96.4	102.7	1.35	[68]
		99.3	103.2 [c]	1.34	[72,73]
			98.4 [c]	1.41	[71,74]
			103.1 [c]	1.34	[71,75]
$[C_6 mim][BF_4]$	146.8 ± 2.7 [16]	118.4	118.5	1.24	[76]
		107.9	113.3	1.30	[68]
			112.0 [c]	1.31	[68,75]
$[C_8 mim][BF_4]$	152.8 ± 2.8 [16]	117.0	118.8	1.29	[77]
		116.7	119.8	1.28	[68]
		142.9	142.3	1.07	[70]
$[C_{10} mim][BF_4]$	158.3 ± 2.8 [16]	132.4			[78]
$[C_{12} mim][BF_4]$	167.3 ± 2.9		132.9	1.26 [e]	[79]
			131.0	1.28 [f]	[79]
$[C_{14} mim][BF_4]$	179.4 ± 3.1		148.5	1.21 [e]	[79]
			137.9	1.30 [f]	[79]
$[C_{16} mim][BF_4]$	180.5 ± 3.5 [d]	143.6	142.7	1.26	[80]
				1.28 ± 0.13	
$[C_4 mim][PF_6]$	146.5 ± 2.6 [13]	96.0	101.3	1.45	[81]
		75.4	96.7 [c]	1.51 [c]	[81,82]
		124.5	99.1 [c]	1.48 [c]	[81,83]
			99.9	1.47	[84]
			97.5 [c]	1.50 [c]	[48,81]
$[C_6 mim][PF_6]$	150.8 ± 2.7 [13]	111.0	111.5	1.35	[85]
		85.7			[86]
$[C_8 mim][PF_6]$	154.9 ± 2.8 [13]	128.7	111.1	1.39 [c]	[86,87]
		128.5	128.4	1.21	[87]
		115.0	115.4	1.34	[88]
				1.41 ± 0.03	
$[C_2 mim][FAP]$ [g]	126.4 ± 1.9 [89]	130.1	135.4	0.93	[90]
		123.3	129.6	0.98	[91]
$[C_6 mim][FAP]$ [g]	141.5 ± 1.9 [89]	158.0	156.0	0.91	[62]
				0.94 ± 0.02	

[a] The definition of symbols is the same as in Table 1. [b] Experimental data on alcohols were absent in this data set. [c] Combination of γ_1^∞ data set of alcohols with the γ_1^∞ data set for *n*-alkanes reported in different papers, as given in the last column. [d] Extrapolated value based on experimental data [16]. [e] Activity coefficients were measure in the liquid phase. [f] Activity coefficients were measured in the liquid-crystal phase. [g] [FAP] = tris(pentafluoroethyl)trifluorophosphate anion.

As can be seen from Table **??**, the factor F_{im} = 1.28 ± 0.13 for $[C_n mim][BF_4]$ and F_{im} = 1.41 ± 0.03 for $[C_n mim][PF_6]$ are closely within their combined uncertainties. Additionally, the chain-length dependence of the F_{im} factors is absent in both series. Moreover, the increase in the number of F atoms in the anion from 4 in $[BF_4]$ to 6 in $[PF_6]$ does not seem to increase the F_{im} factor. In order to reinforce this conclusion, we extended our study with the perfluorinated anion [FAP]. Astonishingly, the factor F_{im} = 0.94 ± 0.02 (see Table **??** for $[C_n mim][FAP]$) does not fulfil our expectations. Hence, it is clear that the factor F_{im} is virtually anion-dependent. However, F_{im} does seem to be chain-length independent (it is explicitly verified in Table **??**, column 5). These two conclusions have been additionally proven with the available γ_1^∞ data sets for $[C_n mim][NO_3]$ (see F_{im}= 1.44 ± 0.06 in Table 5), as well as with the data sets for cyano-containing ionic liquids $[C_n mim][Anion]$ with [SCN], [DCA], [TCM], and [TCB] anions (see Table 6). As shown in this table, the increase in the

number of CN-groups from one in thiocyanate, to two in di-cyano-amide, and three in tri-cyano-methane, does not seem to increase the F_{im} factor ($F_{im} \approx 1.3$ to 1.4 within the combined experimental uncertainties). However, an accumulation of four CN-groups in the [TCB] reduces the factor significantly to the value of $F_{im} = 1.19 \pm 0.08$ (see Table 6 for [C$_n$mim][TCB]). Such a trend is similar to the accumulation of F atoms in the [C$_n$mim][FAP] series (see Table **??**) and should be investigated more closely.

Table 5. [C$_n$mim][NO$_3$] series: comparison of $\Delta_l^g H_m^o$ (298.15 K) values derived according to Equations (5) and (6) with experimental results from conventional methods [a].

IL	$\Delta_l^g H_m^o$(exp)	$\Delta_l^g H_m^o$(GLC)	$\Delta_l^g H_m^o$(HM)	F_{im}	Ref.
[C$_2$mim][NO$_3$]	158.1 ± 5.3 [92]	90.0	96.7	1.63	[93]
[C$_4$mim][NO$_3$]	162.3 ± 5.3 [92]	109.5	115.2	1.41	[94]
[C$_4$mim][NO$_3$]	162.3 ± 5.3 [92]	112.3	111.8	1.45	[95]
[C$_6$mim][NO$_3$]	170.1 ± 5.3 [92]	121.6	120.4 [b]	1.41	[96]
[C$_8$mim][NO$_3$]	177.9 ± 5.3 [92]	136.5	138.9	1.28	[97]
				1.44 ± 0.06	

[a] The definition of symbols is the same as in Table 1. [b] The γ_1^∞ data set for *n*-alkanes were not reported in the original work; they were assessed in this work according to the trend with the chain-length.

Table 6. [C$_n$mim][Anion] series with cyano-containing anions: comparison of $\Delta_l^g H_m^o$ (298.15 K) values derived according to Equations (5) and (6) with experimental results from conventional methods [a].

IL	$\Delta_l^g H_m^o$(exp)	$\Delta_l^g H_m^o$(GLC)	$\Delta_l^g H_m^o$(HM)	F_{im}	Ref.
[C$_2$mim][SCN]	153.6 ± 1.8 [98,99]	100.9	101.2	1.52	[100]
[C$_4$mim][SCN]	156.9 ± 2.5 [98]	116.4	119.9	1.31	[101]
[C$_6$mim][SCN]	164.7 ± 3.0 [98]	122.8	124.4	1.32	[39]
				1.38 ± 0.07	
[C$_2$mim][DCA]	155.6 ± 3.1 [3,5]	102.8	105.2	1.48	[102]
[C$_4$mim][DCA]	162.9 ± 3.4 [3,5]	113.9	122.0	1.34	[103]
				1.41 ± 0.07	
[C$_2$mim][TCM]	140.3 ± 3.0 [5,104]	100.8	106.1	1.32	[105]
[C$_4$mim][TCM]	146.9 ± 3.0 [5,104]	117.7	120.2	1.22	[106]
				1.27 ± 0.05	
[C$_2$mim][TCB]	130.1 ± 2.5 [107]	98.1	100.4	1.30	[108]
		94.4	97.2	1.34	[109]
[C$_6$mim][TCB]	143.0 ± 2.3 [107]	120.8	124.4	1.15	[110]
[C$_{10}$mim][TCB]	157.1 ± 2.5 [107]	155.1	157.9	0.99	[111]
				1.19 ± 0.08	

[a] The definition of symbols is the same as in Table 1. [SCN] = thiocyanate; [DCA] = di-cyanoamide; [TCM] = tri-cyano-methane; and [TCB] = tetra-cyano-borate.

As a final conclusion, it has now been proven that the *HM* approach can generally be used to estimate of $\Delta_l^g H_m^o$(298.15 K) of [C$_n$mim][Anion] by using the anion specific correction factors F_{im} to reconcile "theoretical" and "experimental" values. The variation of the F_{im} factors in the narrow range from 1 to 1.4 localized in this work enables a quick assessment of the general $\Delta_l^g H_m^o$(298.15 K) level, even with the averaged factor $F_{im} = 1.2$. However, these rough estimates could be aggravated by the uncertainties of 5–6 kJ·mol^{-1}, provided that good quality γ_1^∞ data were used in the evaluation. Nevertheless, such agreement between "conventional" $\Delta_l^g H_m^o$(298.15 K) values and those "theoretical" from the *HM* approach can be considered as acceptable, taking into account the experimental uncertainties at the level 2 to 3 kJ·mol^{-1}. The application of the anion-specific F_{im} factors (see Tables 1–3, 5 and 6 and Section 6) can improve agreement between "theoretical" and "experimental" vaporization enthalpies to 2–4 kJ·mol^{-1}. Taking into account the

difficulties described in the introduction when measuring the enthalpies of vaporization of the extremely low-volatile ionic liquids, the *HM* approach is considered a valuable indirect complementary method. It opens a wide window of opportunity to collect a large amount of reliable data for studies on structure–property relationships for ionic liquids. Moreover, the $\Delta_l^g H_m^o$(298.15 K) values derived from the *HM* approach could help to resolve contradictions with the adjustments of vaporization enthalpies from experimental elevated temperatures to the reference temperature T = 298.15 K.

During this study, we have frequently noticed that methanol on the regression plot [δ_1(298.15 K)—Y] was slightly above the general trend (e.g., Figure 1Right and Figure 2Right). At the same time, the experimental point of ethanol met the line better. We use this observation in order to modify the (Heptane-Methanol) approach to the (Heptane-Ethanol) approach (or *HE* approach). To do this, we excluded methanol from the primary γ_1^∞ data sets and recalculated the anion-specific F_{im} factors (see Tables S2–S8). The *HE* approach with the specific F_{im} factors can be helpful in the evaluation of the primary γ_1^∞ data sets, for which methanol was not included or the activity coefficient of methanol is of questionable quality. The reasonable combination of the *HM* and *HE* approaches increases the unbiased flexibility of the γ_1^∞ data sets evaluation and estimation of reliable $\Delta_l^g H_m^o$(298.15 K) values.

7. Outlook for the *HM* Approach

Evaluation of available γ_1^∞ data sets for [$C_n$mim][Anion] series of ionic liquids has generally demonstrated the applicability of the *HM* approach for the independent appraisal of $\Delta_l^g H_m^o$(298.15 K) values. However, there are at least two open questions which should be studied in the future:

— are the correction factors F_{im} designed in this work for [$C_n$mim][Anion] series common for the pyridinium, pyrrolidinium, ammonium, amd phosphonium, etc. based ionic liquids connected to the same anion?

— is the peculiarity observed for the factor F_{im} of the poly-fluorinated and poly-cyano substituted anions connected to the imidazolium cation common for the ionic liquids with other cations? It is easy, if time consuming, to complete this task, as there is already a wealth of γ_1^∞ literature; it will be examined in the forthcoming work. Nonetheless, in critically working with the large amount of primary γ_1^∞ data and having significant experiences with the GLC method, we have generated few essential recommendations for the future experimental work; in the case if the γ_1^∞-values will be deliberately measured for $\Delta_l^g H_m^o$(298.15 K) estimations:

subset of *n*-alkanes should encompass solutes at least from *n*-heptane to *n*-dodecane.
subset of *n*-alcohols should include solutes at least from methanol to *n*-hexanol.
the amount of ionic liquid should be about 35 ÷ 45 mass percent of the support material.
retention times are advisable to measure with the help of two columns of different length (e.g., 50 cm and 100 cm). This advice helps to obtain sharp peaks for both low and high volatility representatives of *n*-alkanes and especially for *n*-alcohol subgroups. The temperature range of the GLC experiment should be as close as possible to the reference temperature T = 298.15 K. The column temperature has to be low enough to escape the solvent tailing (see Figure S1b) for small alkanes. However, the column temperature has to be high enough to avoid the solute peak broadening (see Figure S1c), leading to random errors of time measurements. Implementation of two columns of different length helps to keep the experimental temperature range in optimum.

In our opinion, following these recommendations, a complementary method for reliable assessment of $\Delta_l^g H_m^o$(298.15 K) values will be established.

Supplementary Materials: The following are available online, Figure S1: Typical gas-chromatographic charts from γ_1^∞-measurements, Table S1: Data used for regression of [C_6mim][SCN] solubility parameters, Table S2: Data used for regression of [C_6mim][CF$_3$CO$_2$] solubility parameters, Table S3: Comparison of vaporization enthalpies derived from activity coefficients with experimental results from conventional methods for [$C_n$mim][NTf$_2$] series. Table S4: Comparison of vaporization en-

thalpies derived from activity coefficients with experimental results from conventional methods for [C$_n$mim][NTf$_2$] series. Table S3: Comparison of vaporization enthalpies derived from activity coefficients with experimental results from conventional methods for [C$_n$mim][NTf$_2$] series. Table S3: Comparison of vaporization enthalpies derived from activity coefficients with experimental results from conventional methods for [C$_n$mim][NTf$_2$] series. Table S4: Comparison of vaporization enthalpies derived from activity coefficients with experimental results from conventional methods for [C$_n$mim][CF$_3$CO$_2$] series. Table S5: Comparison of vaporization enthalpies derived from activity coefficients with experimental results from conventional methods for [C$_n$mim][Anion] series with [CF$_3$SO$_3$], [CH$_3$SO$_3$], and [Cl] anions, Table S6: Comparison of vaporization enthalpies derived from activity coefficients with experimental results from conventional methods for [C$_n$mim][Anion] series with fluorine containing anions, Table S7: Comparison of vaporization enthalpies derived from activity coefficients with experimental results from conventional methods for [C$_n$mim][NO$_3$] series, Table S8: Comparison of vaporization enthalpies derived from activity coefficients with experimental results from conventional methods for [C$_n$mim][Anion] series with cyano-containing anions.

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