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A New Method for the Determination of Vaporization Enthalpies of Ionic Liquids at Low Temperatures

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S *Supporting Information*

ABSTRACT: A new method for the determination of vaporization enthalpies of extremely low volatile ILs has been developed using a newly constructed quartz crystal microbalance (QCM) vacuum setup. Because of the very high sensitivity of the QCM it has been possible to reduce the average temperature of the vaporization studies by approximately 100 K in comparison to other conventional techniques. The physical basis of the evaluation procedure has been developed and test measurements have been performed with the common ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)-imide $[C_2mim][NTf_2]$ extending the range of measuring vaporization enthalpies down to 363 K. The results obtained for $[C_2mim][NTf_2]$ have been tested for thermodynamic consistency by comparison with data already available at higher temperatures. Comparison of the temperature-dependent vaporization enthalpy data taken from the literature show only acceptable agreement with the heat capacity difference of $-40\,J\,K^{-1}\,mol^{-1}$. The method developed in this work opens also a new way to obtain reliable values of vaporization enthalpies of thermally unstable ionic liquids.

Higher sensitivity - lower temperature!
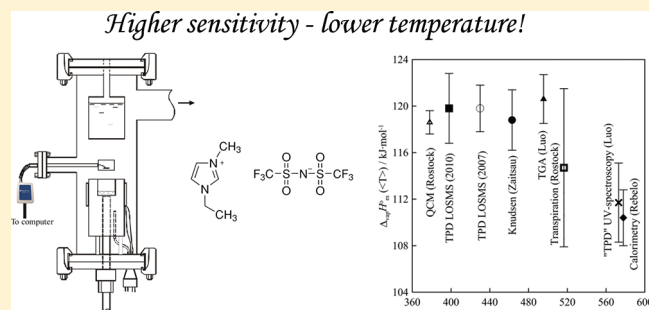
1. INTRODUCTION

Ionic liquids (ILs) have very low but detectable vapor pressure at ambient temperatures. First measurements[1,2] of vapor pressures and quantitative results for enthalpies of vaporization have already been performed before the principal volatility of ILs at elevated temperatures between 473 and 573 K has been demonstrated qualitatively.[3,4] Since then much attention has been paid to the challenging task of measuring vapor pressures of ILs. Traditional techniques for vapor pressure measurements with the exception of the Knudsen method[5,6] have been developed for measuring reliable vapor pressures and vaporization enthalpies for moderately volatile compounds but not for extremely low volatile substances such as ILs. This situation has inspired the development of new experimental methods extending and improving traditional methods toward measurements of reliable vaporization enthalpies, $\Delta_l^g H_m^o$, of ILs. Among these methods are transpiration,[7,8] temperature-programmed desorption with line of sight mass spectrometry (LOSMS),[9–12] thermogravimetry,[13–15] high-temperature spectroscopic technique,[16] and drop microcalorimetry[17] (see Table 1). Each of these methods has peculiarities, advantages, and disadvantages, and their crucial drawback has in common that ILs under study could easily undergo decomposition at elevated temperatures. Typically vaporization processes have been studied between 420 and 600 K.[7–16] In this work we describe a method for determining enthalpies of vaporization of very low volatile ILs using a commercially available quartz crystal microbalance (QCM). The combination of a high-vacuum chamber with the extremely sensitive QCM has turned

out to allow measurements of mass loss rates for ILs at temperatures down to 363 K. In contrast to the conventional Knudsen method, our method is more sensitive since the total open surface is exposed to the QCM under vacuum conditions. This requires also a new physical evaluation procedure different from the Knudsen method. Test measurements have been performed with the common ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide $[C_2mim][NTf_2]$, which has widely been studied in the literature and where experimental data are available obtained by other techniques at higher temperatures.

2. METHODOLOGY OF QCM FOR VAPORIZATION ENTHALPY DETERMINATION FOR ILS

QCMs have been used in microgravimetry for determining very small masses deposited on a quartz crystal surface, since the increasing thickness leads to a change in the resonance frequency.[18–24] It has been shown that the QCM is a sensitive mass sensor for measurements of the *solid* depositions.[25–28] However, there are some intricacies with measurements of *liquid* depositions due to a nonlinear dependency of the frequency change in a case where viscous liquid films of different thicknesses are deposited on the quartz crystal. Moreover, shifts in frequency and bandwidth of the QCM could also be influenced by diverse varieties of

Table 1. Enthalpies of Vaporization of $[C_2mim][NTf_2]$ from the Literature and This Work (kJ mol^{-1})

temperature range, K	T_{av}, K	$\Delta_l^g H_m^\circ$ at T_{av}	$\Delta_l^g H_m^\circ$ at 298.15 K^a	ref
442–484	462.6	118.8 ± 2.7	135.2 ± 2.7	2
300–550	430.0	119.0 ± 2.0	133.2 ± 2.0	9
577.8	577.8	110.4 ± 2.4	138.4 ± 2.4	17
473–523	495.5	120.6 ± 2.1	140.3 ± 2.1	13
499–538	516.5	114.7 ± 6.8	136.5 ± 6.8	7
359–436	398.0	122.0 ± 3.0	132.0 ± 3.0	11
545–600	573.0	109.3 ± 1.7	136.8 ± 1.7	16
362–395	378.2	118.6 ± 1.0	126.6 ± 1.0^b	this work

^{a} Enthalpies of vaporization for ILs were adjusted to 298.15 K with $\Delta_l^g C_{p,m}^\circ = -100$ J K^{-1} mol^{-1}. ^{b} Calculated using eq 8 with $\Delta_l^g C_{p,m}^\circ = -100$ J K^{-1} mol^{-1}.

interactions of the crystal with the liquid sample.[29] The classical "load" on a QCM consists of a thin homogeneous film, which shifts the resonance frequency due to its inertia. Other possible types of loading include semi-infinite viscoelastic media, rough objects contacting the crystal via isolated asperities, mechanically nonlinear contacts, and dielectric films. Thus, for the liquid depositions the knowledge of their density and viscosity under the experimental conditions is required for the correct determination of the mass of the thin film on the quartz crystal,[28−31] but the theoretical treatment is complicated. In contrast, the viscosity of a crystalline sample is very high, and therefore its effect on the frequency shift is very low and determined only by the mass load on the crystal.

Vapor pressure and vaporization enthalpy measurements of low volatile pure organic compounds has been a long-standing goal in our laboratory.[32] During the last years we have focused our efforts on studies of ILs.[2,7,8,10] The high sensitivity of the QCM, offers a method of measuring the mass loss of an IL sample caused by evaporation as function of time. The amount of the IL deposited from the vapor phase on the QCM is a measure not only for the rate of vaporization but also for the equilibrium pressure of the IL. However, very few studies dealing with QCM vapor pressure measurements exist in the literatures which are restricted exclusively to vapor pressure measurements of solids. Surprisingly the QCM method has never been applied for studies of low volatile liquids.

From our knowledge, the first attempt to determine enthalpies of sublimation of some nucleic acids by mass loss rates using a QCM has been made in 1974.[33] In this and in further works[34−36] no absolute values of the vapor pressure have been determined but attempts have been made to derive enthalpies of sublimation from the temperature-dependent change in resonance frequency (df/dt) using the linear correlation $\ln(df/dt \cdot T^{1/2})$ vs $1/T$. Sublimation of samples on to the QCM was performed as a rule from a Knudsen effusion cell or simply from the surface of the sample placed in the open crucible.

A very first trial to obtain absolute vapor pressures for crystalline agrochemicals combining the Knudsen cell with the QCM was made by Goodman.[37] However, it is not clear in this article how the frequency change of the QCM was related to the mass loss of the sample. Several experimental runs with different orifices of the effusion cell are documented by this author, but our analysis of the data revealed a very low reproducibility.

More successful was the work done by Freedman et al.[38] To determine the absolute vapor pressure of solids the frequency change of the QCM was adjusted to the mass uptake through the constant $C = 2.26 \times 10^{-6}$ g^{-1} Hz^{-1} according to calculations made by Sauerbrey.[22] Provided that the Knudsen cell is kept at a fixed distance (and fixed orientation) to the QCM, the measured mass gain rate is related to the vapor pressure by the equation[38]

$$dm/dt = F \times 5.830 \times 10^{-2}$$
$$\times P(\text{Torr})[M(\text{g} \cdot \text{mol}^{-1})/T(K)]^{1/2}$$

where F is a viewing factor representing the fraction of molecules leaving the cell orifice which hit the QCM surface. The F value was calculated in the small angle approximation supposing the validation of cosine law distribution of the molecules leaving the effusion cell orifice. The estimated uncertainty of the vapor pressure determination was ±7%. The device and procedure were tested with benzoic acid, and the absolute vapor pressure values agreed with the reliable experimental data[39−41] within experimental uncertainties.

Another way to determine the sublimation rate of a sample was proposed by Gershanik et al.[42] A solution of 2,4,6-trinitro-toluene in acetonitrile was placed on the surface of a QCM. After evaporation of the acetonitrile the sample was exposed to the continuous air stream. The mass loss rate of trinitro-toluene from microcrystals was directly monitored.

A new Knudsen effusion apparatus with simultaneous gravimetric and quartz crystal microbalance mass loss detection has been described just recently.[43] This modification has also been developed for accurate vapor pressure measurements of solid polyaromatic hydrocarbons (PAHs). To obtain vapor pressures the frequency change of the QCM and the mass loss of the sample in the Knudsen effusion cell were used simultaneously. The frequency change of the QCM and the mass loss of the Knudsen cell (measured gravimetrically) were correlated empirically. The mass loss of the effusion cell during these experiments was typically in the range of 10−20 mg. Because of the much lower vapor pressure of ILs compared to PAH this method is too slow for determining vapor pressures of ILs. We have estimated that few years are required for evaporating 10 mg of any aprotic IL at 380 K under the experimental conditions described by Santos et al.[43] As a consequence we decided to use an open cell instead of the traditional Knudsen cell. This modification provides a large surface for vaporization leading to shorter and acceptable measurement times, usually of 10 to 24 h. Absolute vapor pressures cannot be measured by this method due to unknown empirical parameters of apparatus but enthalpies vaporization of ILs can be determined at lower temperatures not reachable by other techniques used so far. In the focus of the current work has been a development of a new technique for reliable measurements enthalpies of vaporization of very low volatile *liquid* samples such as ILs. For this purpose we have combined evaporation of the sample from the open surface into vacuum with a monitoring of the mass deposition rates using the QCM.

3. EXPERIMENTAL SECTION

3.1. Chemicals. 1-Ethyl-3-methylimidazolium bis(trifluoro-methanesulfonyl)imide $[C_2mim][NTf_2]$ supplied by IoLiTec has been used for our studies. Prior to experiments, the IL was
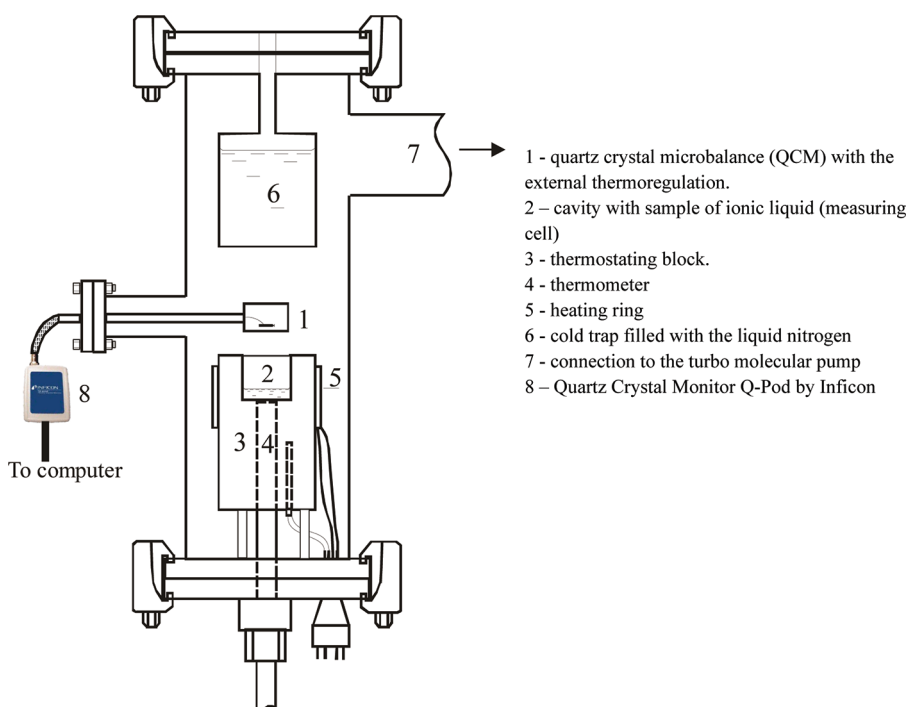
Figure 1. The scheme of the experimental setup.

subjected to vacuum evaporation at 333 K at least for 24 h to remove possible traces of solvents and moisture. The water concentration (<100 ppm) was determined by Karl Fischer titration.

3.2. Equipment. The main parts of the setup are shown in Figure 1: the quartz crystal microbalance (1), the thermostatting block (3) with the measuring cavity (2) inside, the cold trap (6), the connection (7) to the turbo molecular vacuum pump system, and the resonance frequency measuring device Q-Pod by Inficon (8).

The quartz crystal microbalance (part 1 in Figure 1) is placed directly above the cavity containing the IL. The distance between the surfaces of the quartz crystal and of the IL was kept constant at 25 mm. The temperature of the QCM and its holder is kept at 303.0 ± 0.1 K by a Julabo F12-MC thermostat. The resonance frequency of the QCM was measured by a commercial Quartz Crystal Monitor Q-Pod from Inficon. The Q-Pod was kept inside a heat isolating jacket to avoid the results being affected by the fluctuations of room temperature.

The quartz crystal is part of a commercially available sensor BSH-150 by Inficon that measures the vibrational frequency of the quartz crystal. The change in the vibrational frequency of the crystal Δf is directly related to the mass deposition Δm on the crystal according to the Sauerbrey equation[22]

$$\Delta f = -Cf^2 \Delta m S_C^{-1} \qquad (1)$$

where f is the fundamental frequency of the crystal (6 MHz in this case), S_C is the area of the crystal, and $C = 2.26 \times 10^{-6}$ cm^2 g^{-1} Hz^{-1} is a constant considered in the ideal case of the theoretical treatment.[22]

The thermostatting block (part 3 in Figure 1) is made of stainless steel 316Ti which has lower heat conductivity than aluminum but is chemically more inert. This is important for the minimizing of so-called background gases (part of the molecules adsorbed on the internal surface of the measuring block,

evaporating from it, and finally condensing on the QCM). The temperature of the block is controlled to within ±0.02 K by a Watlow PM6C1CA controller equipped with 3-wires resistance thermometer. The temperature inside the block, identical with temperature of the IL, is measured by a Burster 42510 (class A) thermometer (part 4 in Figure 1) connected to a Keithley 2100 multimeter. The thermometer is placed in the pocket of the block (part 3 in Figure 1) as close as possible to the measuring cavity.

The QCM installed in our set up is capable to detect deposition rates ≥50 pg s^{-1}. Preliminary vaporization experiments at 373 K with IL with the classic Knudsen cell have revealed very low evaporation rates even with larger diameters of the effusion orifices. In this work we used a cavity (part 2 in Figure 1) inside the thermostatting block (part 3 in Figure 1) of 24 mm diameter and of 18 mm height serving as the sample holder, i. e., the total surface area of the IL (452 mm^2) was exposed to free vaporization into the vacuum. By use of this procedure enough mass could be collected on the QCM even at temperatures as low as 353 K within a reasonable time.

The working chamber was evacuated by a Varian TPS-Compact turbo molecular pump (part 8 in Figure 1). To prevent the contamination of the turbo molecular pump by any kind of vapors a cold trap (part 7 in Figure 1) filled with the liquid nitrogen was used. The whole construction allows reaching pressures <10^{-5} Pa in the measuring system.

3.3. Measuring Procedure. *3.3.1. Conditioning of the IL Sample.* After filling a sample under study into the cavity in the block (part 3 in Figure 1) possible remainders of any volatile substances have been removed by vacuum treatment at elevated temperatures (383−423 K). First the QCM was covered with aluminum foil to protect the crystal from undesired deposition, and then the cold trap was filled with liquid nitrogen, and the system was evacuated. The temperature of the thermostatting block was set to the highest expected temperature (usually 373−413 K) of mass deposition experiments. The sample was

kept under these conditions for 2−12 h. After venting the system the foil was removed from the QCM. The amount of IL-sample deposited during this time interval on the aluminum foil was analyzed by ATR-IR spectroscopy to detect a possible thermal decomposition of the IL. This conditioning procedure provides an additional purification and degassing of the sample as well as of the surface of the thermostatting block and the measuring chamber. After evacuating the system again, the setup was ready for starting with the measurements. During the mass loss rate determinations, the reproducibility of the first 2−3 sequential series of temperature-dependent mass loss measurements was tested serving as an additional indicator for the absence of possible volatile impurities of the sample.

3.3.2. Determination of the Molar Vaporization Enthalpy. The linear dependence of the change of resonance frequency change and the deposited mass as described by the Sauerbrey equation (eq 1) is valid only for very small mass depositions.[44] The higher the mass deposited on the crystal surface is the larger the deviation from linearity. In contrast to the QCM measurements with any *crystalline* samples where the usual frequency change was possible to keep in the range of 25 kHz,[43] the long-time deposition of the *liquid* sample on the QCM abundant wetting of the quartz crystal begins already at 7 kHz frequency change and as the consequence an irregular fluctuations of the QCM frequencies were observed. In preliminary experiments with IL samples the optimal working interval of the resonance frequency change was set between 1200 to 1300 Hz and for crystalline samples between 2000 to 3000 Hz. According to these benchmarks the duration of the experiment at each temperature was adjusted to get the resonance frequency change of QCM within the interval of 40 to 100 Hz. In doing so, the total shift of the resonance frequency change should not exceed 1300 Hz. The assessed uncertainty of the frequency change determination with the QCM is 0.1 Hz.

Instead of the conventional Knudsen cell we have used an open cavity in this work where the vaporization of the IL into the vacuum takes place. This process is generally related to the Langmuir equation[45] for vaporization from the open surface. The relationship between the change of frequency df/dt and the vaporization enthalpy can be derived in the following way. According to the Clausius−Clapeyron equation, valid for low vapor pressure p, it holds

$$\frac{d \ln p}{dT} = \frac{\Delta_l^g H_m^o(T)}{RT^2} \quad (2)$$

$\Delta_l^g H_m^o(T)$ is the temperature-dependent molar vaporization enthalpy described with sufficient accuracy by

$$\Delta_l^g H_m^o(T) = \Delta_l^g H_m^o(T_0) + \Delta_l^g C_{p,m}^o(T - T_0) \quad (3)$$

T_0 appearing in eq 3 is an arbitrarily chosen reference temperature (which has been chosen to be 298.15 K), and $\Delta_l^g C_{p,m}^o = C_{p,m}^o(g) - C_{p,m}^o(l)$ 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. Integration of eq 2 gives

$$p = p_0 \exp\left(-\frac{\Delta_l^g H_m^o(T_0) - \Delta_l^g C_{p,m}^o T_0}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right)\left(\frac{T}{T_0}\right)^{\Delta_l^g C_{p,m}^o/R} \quad (4)$$

In the process of evaporation of an IL from an open surface with an evaporation rate $\dot{m}_{vap}$ a certain part of evaporated molecules could

return back into the liquid with the condensation rate $\dot{m}_C$. Generally the rate of condensation dm_C/dt of the gaseous compound on the ionic liquid surface S_{IL} in the measuring cavity is according to the kinetic gas theory

$$\dot{m}_C = \frac{dm_C}{dt} = \alpha\sqrt{\frac{M}{2\pi RT}}\,p S_{IL} \quad (5)$$

where M is the molar mass and $\alpha \leq 1$ is the sticking (or condensation[45]) coefficient.

At thermodynamic equilibrium the rate of condensation $\dot{m}_C$ and $\dot{m}_{vap}$ (the rate of evaporation of a liquid) are identical, and we obtain by combining eq 4 and eq 5

$$\dot{m}_{vap} = \frac{dm_{vap}}{dt}$$
$$= F\alpha\sqrt{\frac{M}{2\pi RT}}S_{IL}p_0 \exp\left(-\frac{\Delta_l^g H_m^o(T_0) - \Delta_l^g C_{p,m}^o T_0}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right)\left(\frac{T}{T_0}\right)^{\Delta_l^g C_{p,m}^o/R} \quad (6)$$

The rate of deposition on the QCM, $\dot{m}_C$, is only a certain fraction F of evaporation rate $\dot{m}_{vap}$ from the liquid surface.

Taking the logarithm and collecting all specific values into a constant A we obtain

$$\ln\left(\frac{dm_{vap}}{dt}\sqrt{T}\right) = A - \frac{\Delta_l^g H_m^o(T_0) - \Delta_l^g C_{p,m}^o T_0}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right) + \frac{\Delta_l^g C_{p,m}^o}{R}\ln\left(\frac{T}{T_0}\right) \quad (7)$$

Using eq 1 with $\Delta f/\Delta t \approx \Delta m/\Delta t$ and considering that $\Delta f \ll f$ the final result for evaluating $\Delta_l^g H_m^o(T_0)$ from vapor deposition measurements on the QCM reads

$$\ln\left(\frac{df}{dt}\sqrt{T}\right) = A' - \frac{\Delta_l^g H_m^o(T_0) - \Delta_l^g C_{pm}^o T_0}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right) + \frac{\Delta_l^g C_{pm}^o}{R}\ln\left(\frac{T}{T_0}\right) \quad (8)$$

with an empirical constant $A' = A + \ln(F)$ and $F = S_C/S_{IL}$ being approximately the ratio of the surface of the QCM to surface of the IL in the cavity. Equation 8 is the basis for evaluating $\Delta_l^g H_m^o(T)$ from temperature-dependent measurements of df/dt by adjusting A' and $\Delta_l^g H_m^o(T_0)$ using a known value of $\Delta_l^g C_{p,m}^o$.

To detect and avoid possible effect of impurities on the measured frequency loss rate df/dt a typical experiment has been carried out as a series of experimental runs. Each step consisted of 6−7 constant temperature points of mass loss rate determinations. Reproducible results obtained from eq 8 for several runs indicated reliable data sets. The experiment was finished when the enthalpy of vaporization, $\Delta_l^g H_m^o(T_0)$ calculated from eq 8 for the repeated runs agreed within $\pm(0.1-1)$ kJ·mol^{-1}. To detect possible decomposition, the residual IL in the cavity and the IL-deposit on QCM were analyzed by ATR-IR spectroscopy (see Figure S3 of the Supporting Information). Figure S1 of the Supporting Information shows an example for measured values of df/dt vs reciprocal temperature to which eq 8 has been adjusted. To assess the uncertainty of the vaporization enthalpy, the experimental data were approximated with the eq 8 using the method of least-squares. Scattering of the QCM experimental data related to the fitting correlation with eq 8 is shown in Figure S2 of the Supporting Information, revealing an uncertainty of

Table 2. Results of the Temperature Dependence of Frequency Shift Velocity df/dt of the QCM for $[C_2mim][NTf_2]$ and Vaporization Enthalpies $\Delta_l^g H_m^o(T)$

run	T/K	df/dt (Hz s^{-1})	T^{-1} (K^{-1})	$\ln(df/dt \cdot T^{1/2})$	$\Delta_l^g H_m^o(T)^a$ (kJ mol^{-1})	$\Delta_l^g H_m^o(T)^b$ (kJ mol^{-1})	$\Delta_l^g H_m^o(T)^c$ (kJ mol^{-1})
1	392.24	0.2723	0.002549	1.685	117.1	118.0	116.7
	387.24	0.1718	0.002582	1.218	117.6	118.2	117.3
	382.23	0.1069	0.002616	0.7373	118.1	118.4	118.0
	377.24	0.06569	0.002651	0.2436	118.6	118.6	118.7
	372.24	0.03977	0.002686	−0.2648	119.1	118.8	119.3
	367.24	0.02374	0.002723	−0.7876	119.6	119.0	120.0
	362.25	0.01399	0.002761	−1.323	120.1	119.2	120.7
2	394.67	0.3400	0.002534	1.910	116.9	117.9	116.3
	389.72	0.2163	0.002566	1.452	117.4	118.1	117.0
	384.78	0.1365	0.002599	0.9846	117.9	118.3	117.7
	379.76	0.08408	0.002633	0.4938	118.4	118.5	118.3
	374.77	0.05148	0.002668	−0.003452	118.9	118.7	119.0
	369.76	0.03082	0.002704	−0.5233	119.4	118.9	119.7
	364.75	0.01823	0.002742	−1.055	119.9	119.1	120.3

^{a} Calculated using eq 8 with $\Delta_l^g C_{p,m}^o = -100$ J K^{-1} mol^{-1}. Equation 8 for the fitting of the experimental data: $\ln((df/dt)(T)^{1/2}) = -(84.38/R) - (156373/R)((1/T) - (1/T_0)) - (100/R)\ln(T/T_0)$. ^{b} Calculated using eq 8 with $\Delta_l^g C_{p,m}^o = -40$ J K^{-1} mol^{-1}. Equation 8 for the fitting of the experimental data: $\ln((df/dt)(T)^{1/2}) = -(82.57/R) - (133690/R)((1/T) - (1/T_0)) - (40/R)\ln(T/T_0)$. ^{c} Calculated using eq 8 with $\Delta_l^g C_{p,m}^o = -133.6$ J K^{-1} mol^{-1}. Equation 8 for the fitting of the experimental data: $\ln((df/dt)(T)^{1/2}) = -(85.40/R) - (169075/R)((1/T) - (1/T_0)) - (133.6/R)\ln(T/T_0)$.

±0.6%. The uncertainty in $\Delta_l^g H_m^o$ value is usually assumed to be identical with the average deviation of experimental values from this linear correlation. In the case of $[C_2mim][NTf_2]$ the uncertainty of $\Delta_l^g H_m^o$ value turns out to be within ±0.1 kJ mol^{-1} (the twice standard deviation was used as the uncertainty), which reflects a high reproducibility of our new method. However, taking into account temperature and pressure fluctuations in the measuring system, the combined uncertainties of $\Delta_l^g H_m^o$ measured with the QCM have been suggested of 1.0 kJ mol^{-1}.

4. RESULTS AND DISCUSSION

A careful validation of the experimental procedure to determine enthalpies of vaporization of ILs with the QCM techniques has been made using the ionic liquid $[C_2mim][NTf_2]$ as an example. Our experimental results on $[C_2mim][NTf_2]$ are presented in Table 2. This IL has been studied in the past using the Knudsen method[2] between 442 and 481 K, the transpiration method[7] (499 to 538) K, the temperature-programmed desorption and line of sight mass spectrometry (LOSMS)[9,11] at (400−550) K, drop microcalorimetry[17] (at T_{av} = 577.8 K), and thermogravimetry[13] at T_{av} = 495.5 K, providing a suitable test system for comparison. Enthalpies of vaporization for $[C_2mim][NTf_2]$ available from the literature are collected in Table 1 and also shown in Figure 2. For comparison with the literature the enthalpy of vaporization of $[C_2mim][NTf_2]$ at the average temperature 378 K, $\Delta_l^g H_m^o$(378 K) = (118.6 ± 0.1) kJ mol^{-1} was derived (see Table 1, last line) using the data given in Table 2. It should be noticed that the molar enthalpies of vaporization $\Delta_l^g H_m^o(T)$ for $[C_2mim][NTf_2]$ determined in these previous works were derived from the experiments at temperatures substantially higher than those in this work (see Table 1).

For the sake of comparison, enthalpies of vaporization for $[C_2mim][NTf_2]$ were also adjusted to the reference temperature 298.15 K with the acknowledged[3,7,9] value $\Delta_l^g C_{p,m}^o = -100$ J K^{-1} mol^{-1} (difference between heat capacities of the liquid $C_{p,m}^o$(l) and the gaseous $C_{p,m}^o$(g) phases of an ionic liquid). We use
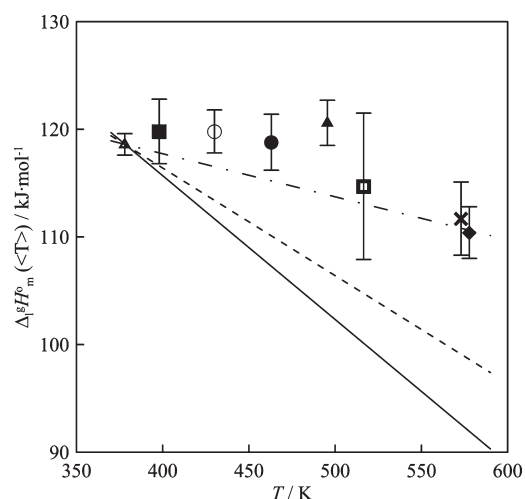

Figure 2. Enthalpies of vaporization of $[C_2mim][NTf_2]$ obtained by different methods at their mean temperatures T_{av} (see Table 1). (●) Knudsen method,[2] (○) LOSMS,[9] (■) LOSMS at maximum sensitivity and in the lowest temperature interval,[11] (□) transpiration method,[7] (♦) drop calorimetry,[17] (▲) thermogravimetry,[13] (△) QCM (this work), (×) UV spectroscopic investigation of the gaseous phase for ionic liquids.[16] (Dot-dashed line) Temperature dependence of vaporization enthalpy was treated with $\Delta_l^g C_{p,m}^o = -40$ J K^{-1} mol^{-1}. (Dashed line) Temperature dependence of vaporization enthalpy was treated with $\Delta_l^g C_{p,m}^o = -100$ J K^{-1} mol^{-1} (Solid line) Temperature dependence of vaporization enthalpy was treated with $\Delta_l^g C_{p,m}^o = -133.6$ J K^{-1} mol^{-1}.

this $\Delta_l^g C_{p,m}^o$ value in the current work in order to keep consistency with our previous work. Results at 298.15 K collected in Table 1 show no satisfying agreement with our new result when $\Delta_l^g C_{p,m}^o = -100$ J K^{-1} mol^{-1} was used (see Figure 2). The discrepancies at 298.15 K are arising apparently due to the long way of extrapolation of the measured $\Delta_l^g H_m^o$ at T_{av} to the reference temperature. Figure 2 reveals that comparison of the data fitted by eq 8 with the temperature-dependent data $\Delta_l^g H_m^o(T)$ taken from the

literature show only acceptable agreement with the $\Delta_l^g C_{p,m}° = -40$ J K^{-1} mol^{-1}. The recommended literature value of $\Delta_l^g C_{p,m}° = -100$ J K^{-1} mol^{-1} nowadays is commonly used for all possible ILs. It is based[7,10] on reliable experimental data of $C_{p,m}°(l)$ and on theoretical value of $C_{p,m}°(g)$ calculated by DFT methods. It is also possible to use for adjustment to 298.15 K the value of $\Delta_l^g C_{p,m}° = -133.6$ J K^{-1} mol^{-1}, which was derived for $[C_2mim][NTf_2]$ using the selected experimental value $C_{p,m}°(l) = 506.3$ J K^{-1} mol^{-1}[46] and $C_{p,m}°(g) = 372.7$ J K^{-1} mol^{-1} calculated using the B3LYP/6-311++G-(3df,3pd) functional.[47] But according to Figure 2 the disagreement with the available experimental data is even larger in this case. Such a disagreement indicates that the current recommended value of $\Delta_l^g C_{p,m}° = -100$ J K^{-1} mol^{-1} commonly used in the literature for extrapolation to the reference temperature is generally overestimated and the reasonable value of $\Delta_l^g C_{p,m}°$ for $[C_2mim][NTf_2]$ seems to be at the level of -40 J K^{-1} mol^{-1}. It is difficult to decide whether the uncertainties of experimental results on $\Delta_f^g H_m°(T)$ taken from the literature are the reason for this disagreement or doubtful calculations of $C_{p,m}°(g)$ of $[C_2mim][NTf_2]$.

■ CONCLUSION

We have developed the new method for the reliable determination of vaporization enthalpies of extremely low volatile ionic liquids using the QCM. Because of the very high sensitivity of the QCM it has been possible to reduce the average temperature of the vaporization studies by approximately 100 K in comparison to other conventional techniques.

■ ASSOCIATED CONTENT

ⓢ **Supporting Information.** Figures depicting the experimental data set (df/dt), deviation of mass deposit rate, and IR spectra during enthalpy of vaporization investigation for $[C_2mim]$-$[NTf_2]$. This material is available free of charge via the Internet at http://pubs.acs.org.

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