

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/225275327>

An elegant access to formation and vaporization enthalpies of ionic liquids by indirect DSC experiment and "in silico" calculations

ARTICLE *in* CHEMICAL COMMUNICATIONS · JUNE 2012

Impact Factor: 6.83 · DOI: 10.1039/c2cc31504a · Source: PubMed

CITATIONS

5

READS

47

6 AUTHORS, INCLUDING:



Dzmitry Zaitsau

Kazan (Volga Region) Federal University

54 PUBLICATIONS 964 CITATIONS

SEE PROFILE



Christoph Schick

University of Rostock

418 PUBLICATIONS 6,680 CITATIONS

SEE PROFILE



Sai Jayaraman

Massachusetts Institute of Technology

12 PUBLICATIONS 106 CITATIONS

SEE PROFILE



Edward J Maginn

University of Notre Dame

204 PUBLICATIONS 9,452 CITATIONS

SEE PROFILE

ChemComm

This article is part of the

Ionic Liquids web themed issue

Guest editors: Robin D. Rogers, Douglas MacFarlane
and Suojang Zhang

All articles in this issue will be gathered together
online at

www.rsc.org/ionic



Cite this: *Chem. Commun.*, 2012, **48**, 6915–6917

www.rsc.org/chemcomm

COMMUNICATION

An elegant access to formation and vaporization enthalpies of ionic liquids by indirect DSC experiment and “*in silico*” calculations†Sergey P. Verevkin,^{*a} Dzmitry H. Zaitsau,^a Vladimir N. Emel'yanenko,^a Christoph Schick,^a Saivenkataraman Jayaraman^b and Edward J. Maginn^c

Received 28th February 2012, Accepted 15th May 2012

DOI: 10.1039/c2cc31504a

We used DSC for determination of the reaction enthalpy of the synthesis of the ionic liquid [C₄mim][Cl]. A combination of DSC and quantum chemical calculations presents a new, indirect way to study thermodynamics of ionic liquids. The new procedure was validated with two direct experimental measurements and MD simulations.

Ionic liquids (ILs) are neoteric materials which have garnered attention from both academia and industry during the last decade. Alkyl halides are widely used for ILs synthesis as alkylating agents in quaternization reactions, since they are cheap and easily available. The formation reactions are irreversible. As a consequence, systematic studies of the IL synthesis reactions, and the measurement and computation of reaction enthalpies, are of importance in process design. Reaction enthalpies, $\Delta_r H^\circ_m$, can be reliably measured using traditional reaction calorimetry.¹ However, calorimetric study in practice turns out to be a complex and challenging procedure where measurements of dissolution and fusion enthalpies of the reaction participants are required.² Alternatively, differential scanning calorimetry (DSC) seems to be a suitable experimental tool for measuring $\Delta_r H^\circ_m$.³ DSC is nowadays broadly used for determination of enthalpies of phase transitions and for heat capacity measurements.⁴ DSC offers definite advantages in comparison to traditional reaction calorimetry, such as the requirement of smaller quantities of experimental samples (a few milligrams), swiftness of sample scan, precise temperature control, and commercial availability of the device. Over the last decade, we have recognised an additional advantage of using DSC to analyze ILs, namely a possibility to measure a broader range of thermochemical properties indirectly. Our longstanding interest in ionic liquids is focused on providing systematic thermodynamic data.^{5,6,7} The traditional way to obtain enthalpies of formation is to use oxygen bomb calorimetry.⁵ However, reliable data can be obtained only if

the final products of the reaction (ideally CO₂ and H₂O) are well defined, and completeness of combustion is achieved. These requirements are not satisfied by the most popular ILs due to the presence of F, Cl, Br, and S among common anions like [BF₄] or [NTF₂]. This is compounded by the challenge in determining the degree of oxidation of hetero-elements. Moreover, combustion of simpler Cl, Br, or S containing ILs, (for instance, the [C_nmim] cation and the anions Cl, Br or SCN) necessitates a special rotating bomb combustion calorimetry which includes a complex analysis of the oxidation products.⁸ In all such situations, DSC offers a feasible alternative. For example, instead of sophisticated combustion experiments with [C₄mim][Cl], DSC can be used to measure the enthalpy of the following reaction:



According to Hess' Law, reaction enthalpy is defined as the difference between enthalpies of formation ($\Delta_f H^\circ_m$) of the products and reactants:

$$\begin{aligned} \Delta_r H^\circ_m (\text{liq}) &= \Delta_f H^\circ_m ([\text{C}_4\text{mim}][\text{Cl}], \text{liq}) \\ &- \Delta_f H^\circ_m (\text{1-Me-im, liq}) - \Delta_f H^\circ_m (\text{C}_4\text{H}_9\text{Cl, liq}) \quad (2) \end{aligned}$$

Once the $\Delta_r H^\circ_m$ (1) is measured by DSC, the $\Delta_f H^\circ_m ([\text{C}_4\text{mim}][\text{Cl}], \text{liq})$, is known provided that the $\Delta_f H^\circ_m$ of the precursors are known. This was realized by studying reaction (1) using a computer-controlled Mettler-Toledo 822 heat flux DSC. The reaction enthalpy of (2) was determined to be $(-78.6 \pm 0.8) \text{ kJ mol}^{-1}$ in a series of four DSC runs under optimized conditions³ (Table S1 of ESI).†

Enthalpies of formation, $\Delta_f H^\circ_m$, from DSC measurements: using the experimental $\Delta_r H^\circ_m$ value of the precursors of reaction (1) at 298 K: $\Delta_f H^\circ_m (\text{1-Me-imidazole, liq}) = (70.7 \pm 1.1) \text{ kJ mol}^{-1}$,⁹ and $\Delta_f H^\circ_m (\text{C}_4\text{H}_9\text{Cl, liq}) = -(188.2 \pm 1.2) \text{ kJ mol}^{-1}$,¹⁰ the enthalpy of formation of the IL $\Delta_f H^\circ_m ([\text{C}_4\text{mim}][\text{Cl}], \text{liq})$ in the hypothetical liquid state calculated from eqn (2) is:

$$\begin{aligned} \Delta_f H^\circ_m ([\text{C}_4\text{mim}][\text{Cl}], \text{liq}) &= (-78.6) + (70.7) + (-188.2) \\ &= (-196.1 \pm 1.8) \text{ kJ mol}^{-1} \quad (3) \end{aligned}$$

As a matter of fact, the ionic liquid [C₄mim][Cl] is not liquid at room temperature. It is a solid with a melting point of $341.8 \pm 0.2 \text{ K}$ and the molar fusion enthalpy $\Delta_{\text{fus}} H^\circ_m = 21.7 \pm 0.5 \text{ kJ mol}^{-1}$ at T_{fus} . When adjusted to 298 K

^a Department of Physical Chemistry, University of Rostock, Dr-Lorenz-Weg. 1, 18059 Rostock, Germany.
E-mail: sergey.verevkin@uni-rostock.de; Fax: +49 381 498 6524;
Tel: +49 381 498 6508

^b Sandia National Laboratories, Albuquerque, New Mexico 87185, USA

^c Department of Chemical and Biomolecular Engineering, University of Notre Dame, Notre Dame, IN 46556, USA

† Electronic supplementary information (ESI) available: Details of experimental procedures and calculations. See DOI: 10.1039/c2cc31504a

$\Delta_{\text{fus}}H^\circ_{\text{m}} = 18.6 \pm 0.5 \text{ kJ mol}^{-1}$ (see details in ESI†) and hence, the enthalpy of formation in the solid state is given by:

$$\Delta_f H^\circ_{\text{m}}([\text{C}_4\text{mim}][\text{Cl}], \text{ s}, 298 \text{ K}) \\ = (-196.1) - (18.6) = (-214.7 \pm 1.9) \text{ kJ mol}^{-1} \quad (4)$$

It should be emphasized that this enthalpy of formation of the solid ([C₄mim][Cl], s) has been obtained indirectly in several steps but by using only experimental data. But, what is the value of this solid phase enthalpy of formation?

Enthalpies of formation, $\Delta_f H^\circ_{\text{m}}$ – Quo vadis? A few important aspects could be mentioned in this context. First, with the help of $\Delta_f H^\circ_{\text{m}}(\text{s})$ it is possible to assess a lattice potential energy (U_{POT}) and lattice enthalpy (ΔH_{L}) of an ionic solid. This is a measure of the strength of bonds in that ionic compound. It is usually defined as the enthalpy of formation of the ionic compound from gaseous ions:^{11,12}

$$U_{\text{POT}}([\text{C}_4\text{mim}][\text{Cl}]) = \Delta_f H^\circ_{\text{m}}([\text{C}_4\text{mim}]^+, \text{ g}) + \Delta_f H^\circ_{\text{m}}([\text{Cl}]^-, \text{ g}) \\ - 2RT - \Delta_f H^\circ_{\text{m}}([\text{C}_4\text{mim}][\text{Cl}], \text{ s}) \quad (5)$$

Lattice potential energy is a dominant term in the thermodynamic analysis of the existence and stability of ionic solids. Direct experimental determination is generally not possible since, in practice, the crystalline solid dissociates into atoms and *not* into gaseous ions, as is required in the lattice energy evaluation.¹³ By combining experimental data, empirical correlations, and quantum chemical calculations, Born–Fajans–Haber cycles can be constructed to gain a deeper insight into reaction or phase transition thermodynamics.^{14,15} A simple “volume-based thermodynamics” (VBT) procedure was developed recently for the evaluation of U_{POT} , which relies only on the chemical formula, ionic charges and molecular volume (or density) of the ionic compounds.^{12,16} However, for a proper validation of the VBT-equation the extended data set of the experimental $\Delta_f H^\circ_{\text{m}}(\text{s})$ derived by using calorimetry is essential, and DSC can be an appropriate tool for rapid accumulation of the experimental data.

The second valuable application of the $\Delta_f H^\circ_{\text{m}}(\text{liq})$ and $\Delta_f H^\circ_{\text{m}}(\text{s})$ data for ILs can be for the design and synthesis of new energetic materials. $\Delta_f H^\circ_{\text{m}}$ is a key property which is used to assess potential performance in technology applications of high-energy-density materials.^{17,18} Taking into account restricted possibilities for safe experimental studies of high-energy materials, a reasonable combination of experimental and “*in silico*” studies offers a critical advantage. Thus development of any procedure suitable for reliable assessment of $\Delta_f H^\circ_{\text{m}}$ of energetic ILs could save much time and effort in the synthesis and development of new energetic materials. A test set of reliable experimental $\Delta_f H^\circ_{\text{m}}$ for ILs containing a broad range of common cations and anions can be collected by using the DSC technique according to eqn (1)–(4).

Vaporization enthalpy from $\Delta_f H^\circ_{\text{m}}$: the third valuable application of the enthalpic data derived from DSC is the ability to obtain an indirect estimate of the $\Delta_f^\circ H^\circ_{\text{m}}$ of ILs. A lot of methods, including Knudsen effusion, transpiration, TGA, UV, LOSMS, and so on, have been reported to determine the vaporization enthalpy of ILs.^{6,21} However, reliable direct measurement of $\Delta_f^\circ H^\circ_{\text{m}}$ remains a challenging task due to elevated experimental temperatures.^{5–7} A valuable procedure whereby $\Delta_f^\circ H^\circ_{\text{m}}$ of ILs can be obtained indirectly using a combination of traditional combustion calorimetry and modern high-level quantum chemical computations has been suggested recently.⁵ $\Delta_f^\circ H^\circ_{\text{m}}$ is obtained as

the difference between $\Delta_f H^\circ_{\text{m}}(\text{g})$ of the IL as calculated using *first-principles* methods and $\Delta_f H^\circ_{\text{m}}(\text{liq})$ as obtained from high precision combustion calorimetry, where:

$$\Delta_f^\circ H^\circ_{\text{m}} = \Delta_f H^\circ_{\text{m}}(\text{g}) - \Delta_f H^\circ_{\text{m}}(\text{liq}) \quad (6)$$

This procedure has been successfully tested with different imidazolium-based ILs.^{5,19} Excellent agreement of the value derived from eqn (6) with the experimental $\Delta_f^\circ H^\circ_{\text{m}}$ has proved the thermodynamic consistency of both the experimental and theoretical methods. Such a new procedure has opened a new indirect way to obtain $\Delta_f^\circ H^\circ_{\text{m}}$ of ILs which have not been available so far. Unfortunately, this new procedure cannot serve for a rapid accumulation of $\Delta_f^\circ H^\circ_{\text{m}}$ for ILs. The restriction is mainly due to the sophisticated and time-consuming combustion experiments, which have to be performed on highly pure (99.9%) samples of ILs. But in contrast to the combustion calorimetry, the DSC experiments have less demanding requirements for purities of the precursors involved in eqn (1). That is why the $\Delta_f H^\circ_{\text{m}}$ obtained *via* eqn (3) from the DSC measurements could be now used instead of the combustion results and to bring a new life into eqn (6). Thus, in this work we have extended the procedure combining high-level quantum chemical calculations with the results from DSC as a valuable thermochemical option to compute $\Delta_f^\circ H^\circ_{\text{m}}$. The $\Delta_f^\circ H^\circ_{\text{m}}$ for the [C₄mim][Cl] was calculated as eqn (6):

$$\Delta_f^\circ H^\circ_{\text{m}} = (-43.5) - (-196.1) = (152.6 \pm 4.4) \quad (7)$$

where $\Delta_f H^\circ_{\text{m}}(\text{liq})$ was derived from DSC calorimetry and $\Delta_f H^\circ_{\text{m}}(\text{g}) = (-43.5 \pm 4.0) \text{ kJ mol}^{-1}$ was calculated by first-principles calculations (CBS-QB3 method).

Vaporization enthalpy from DSC enthalpies of reaction, $\Delta_r H^\circ_{\text{m}}$: the indirect option to determine $\Delta_f^\circ H^\circ_{\text{m}}$ using eqn (6) suffers from one input requirement: it is based on $\Delta_f H^\circ_{\text{m}}(\text{g})$, which is calculated using quantum chemical methods. There are some ambiguities with respect to procedures for converting results of first-principles calculations (total energies E_0 at $T = 0 \text{ K}$ and enthalpies H_{298} at $T = 298 \text{ K}$) into the desired value of $\Delta_f H^\circ_{\text{m}}(\text{g})$. It is well established that in standard Gaussian-*n* theories theoretical $\Delta_f H^\circ_{\text{m}}(\text{g})$ are calculated through atomization reactions, isodesmic and bond separation reactions. However, it has been observed²⁰ that $\Delta_f H^\circ_{\text{m}}(\text{g})$ calculated from the standard atomization procedure systematically deviate very often from the available experimental results.²⁰ Hence we are somewhat reticent to use atomization reactions, isodesmic and bond separation reactions to obtain $\Delta_f H^\circ_{\text{m}}(\text{g})$ of ILs. All the same, using DSC we have measured the experimental $\Delta_r H^\circ_{\text{m}}(\text{l})$ *e.g.* for [C₄mim][Cl] according to eqn (2). The $\Delta_r H^\circ_{\text{m}}$ for (1) in the gas phase could be obtained from the first-principles calculations as shown in eqn (8):



We have calculated the H_{298} at $T = 298 \text{ K}$ for all reaction participants of reaction (1) using the CBS-Q3B approach. According to Hess’ Law, the enthalpy of this reaction is calculated as follows:

$$\Delta_r H^\circ_{\text{m}}(\text{g}) = H_{298}([\text{C}_4\text{mim}][\text{Cl}], \text{ g}) - H_{298}(1\text{-Me-imidazole, g}) \\ - H_{298}(\text{C}_4\text{H}_9\text{Cl, liq}) = (-14.9 \pm 4.0) \text{ kJ mol}^{-1} \quad (9)$$

It is important to emphasise that the $\Delta_f H^\circ_{\text{m}}(\text{g})$ was obtained using quantum chemical methods *directly* from the calculated H_{298} bypassing the conventional calculation of the $\Delta_f H^\circ_{\text{m}}$ with the help of atomization or isodesmic procedures. As a consequence

of this manoeuvre, the resulting $\Delta_r H_m^\circ(\text{g})$ is not affected at all by the choice and the quality of the auxiliary quantities commonly required for atomization or bond separation reactions. Having established $\Delta_r H_m^\circ(\text{liq})_{\text{exp}}$ from the experiment and $\Delta_r H_m^\circ(\text{g})$ from quantum chemistry, we have derived the $\Delta_f H_m^\circ$ (e.g. for IL = [C₄mim][Cl]) provided that the following balance holds:

$$\Delta_r H_m^\circ(\text{liq}) = \Delta_r H_m^\circ(\text{g}) - \Delta_f H_m^\circ \quad (10)$$

The experimental $\Delta_r H_m^\circ$ was calculated using Hess' Law:

$$\begin{aligned} \Delta_r H_m^\circ(\text{liq})_{\text{exp}} &= [\Delta_r H_m^\circ(\text{g, IL}) - \Delta_f H_m^\circ(\text{IL})] \\ &\quad - [\Delta_r H_m^\circ(\text{g, 1-Me-im}) - \Delta_f H_m^\circ(\text{1-Me-im})] \\ &\quad - [\Delta_r H_m^\circ(\text{g, C}_4\text{H}_9\text{Cl}) - \Delta_f H_m^\circ(\text{C}_4\text{H}_9\text{Cl})] \end{aligned} \quad (11)$$

The $\Delta_f H_m^\circ$ of the IL has been obtained from eqn (11):

$$\begin{aligned} \Delta_f H_m^\circ(\text{IL, 298 K}) &= -\Delta_r H_m^\circ(\text{liq})_{\text{exp}} + \Delta_r H_m^\circ(\text{g}) \\ &\quad + \Delta_f H_m^\circ(\text{1-Me-im}) + \Delta_f H_m^\circ(\text{C}_4\text{H}_9\text{Cl}) \\ &= -(-78.6) + (-14.9) + (55.0) + (33.5) \\ &= 152.2 \pm 4.1 \text{ kJ mol}^{-1} \end{aligned} \quad (12)$$

So, using the theoretical value $\Delta_r H_m^\circ(\text{g})$ calculated with CBS-QB3 in the gas phase and $\Delta_f H_m^\circ$ at 298 K of precursors $\Delta_f H_m^\circ(\text{1-Me-im}) = 55.0 \pm 0.3 \text{ kJ mol}^{-1}$,⁹ and $\Delta_f H_m^\circ(\text{C}_4\text{H}_9\text{Cl}) = 33.5 \pm 0.1 \text{ kJ mol}^{-1}$,¹⁰ and $\Delta_r H_m^\circ(\text{liq})_{\text{exp}}$ measured using the DSC in the liquid phase, the $\Delta_f H_m^\circ$ of [C₄mim][Cl] has been calculated. Comparison of the $\Delta_f H_m^\circ$ derived using two different procedures (i.e. eqn (2) and (7)) shows that both methods provide values in very close agreement with one another. We recommend eqn (12), however, because the $\Delta_r H_m^\circ(\text{g})$ for this procedure has been calculated *directly* from H_{298} avoiding any procedure for converting quantum-chemical results into enthalpy of formation.

$\Delta_f H_m^\circ$ from direct QCM and TGA measurements: using indirect means to assess thermodynamic properties requires careful validation of the procedure with reliable experimental values. We have recently developed two experimental methods for the determination of $\Delta_f H_m^\circ$ of extremely low volatility ILs: quartz-crystal microbalance (QCM)⁶ and thermogravimetric analysis (TGA).²¹ We used both these methods to measure $\Delta_f H_m^\circ$ of [C₄mim][Cl] (for details see Tables S2 and S3 in ESI†). The values (adjusted to the reference temperature 298 K using the commonly acknowledged $\Delta_f C_{p,m}^\circ = -100 \text{ J mol}^{-1} \text{ K}^{-1}$) are as follows: $153.5 \pm 1.5 \text{ kJ mol}^{-1}$ from QCM and $151.3 \pm 1.7 \text{ kJ mol}^{-1}$ from TGA. It is quite obvious that the experimental $\Delta_f H_m^\circ$ are indistinguishable within the boundaries of the experimental uncertainties. At the same time the direct experimental values are also in excellent agreement with those indirectly derived from the DSC measurements by using eqn (2) and (12). This test convincingly demonstrates the ability of the DSC method to provide reliable indirect vaporization enthalpies of ILs.

$\Delta_f H_m^\circ$ from molecular dynamics simulations: as an additional test to establish consistency of the direct and indirect $\Delta_f H_m^\circ$, we have also used molecular dynamics simulations to compute pure, “*in silico*”, $\Delta_f H_m^\circ$. These were computed for [C₄mim][Cl] over a temperature range of 343–383 K (see Table S4 in ESI†) using the method outlined.²² The $\Delta_f H_m^\circ$ at the lowest temperature 343 K was calculated to be $147.4 \text{ kJ mol}^{-1}$. Akin to the experimental QCM and TGA results, this value was adjusted to 298 K as $\Delta_f H_m^\circ(\text{[C}_4\text{mim][Cl]}) = 151.6 \pm 0.3 \text{ kJ mol}^{-1}$. Comparison of the experimental and “*in silico*” $\Delta_f H_m^\circ$ shows very good agreement. Please refer to the ESI† for force field and computational details.

Summary of benefits of using DSC for indirect evaluation of $\Delta_f H_m^\circ$: there are several very important advantages of using the DSC technique for the indirect evaluation of the $\Delta_f H_m^\circ$ of ILs:

- $\Delta_r H_m^\circ(\text{liq})_{\text{exp}}$ measurements using DSC are quick and less demanding as compared to combustion calorimetry;
- purity requirements for the chemicals are less rigorous
- $\Delta_r H_m^\circ(\text{g})$ is obtained using first principles *directly* from calculated H_{298} (avoiding the usual calculation of $\Delta_r H_m^\circ(\text{g})$ with the help of atomization or isodesmic procedures);
- $\Delta_f H_m^\circ$ of the starting chemicals are well known or easy to measure.
- DSC calorimeter is available as basic equipment in the labs working with ILs.

In conclusion, we have successfully coupled DSC measurements with “*in silico*” quantum chemical methods. This alliance suggests a new thermochemical option for rapid accumulation of data on $\Delta_f H_m^\circ$ and $\Delta_r H_m^\circ$ for a series of imidazolium, pyridinium, and pyrrolidinium based ILs. MD simulations can also be used for reliable calculation of $\Delta_f H_m^\circ$ of ILs.

This work has been supported by the German Science Foundation (DFG) in the frame of the priority program SPP 1191 “Ionic Liquids”. Additional support was provided by the US Air Force Office of Scientific Research under AFOSR Award FA9550-10-1-0244.

Notes and references

- 1 *Thermochemistry of Organic and Organometallic Compounds*, ed. J. D. Cox and G. Pilcher, Academic Press, London, 1970.
- 2 Y. U. Paulechka, A. G. Kabo and A. V. Blokhin, *J. Phys. Chem. B*, 2009, **113**, 14742–14746.
- 3 S. P. Verevkin, V. N. Emel'yanenko, Dz. H. Zaitsau, R. V. Ralys and Ch. Schick, *J. Phys. Chem. B*, 2012, **116**, 4276–4285.
- 4 *Differential Scanning Calorimetry*, ed. G. Höhne and W. Hemminger and H.-J. Flammersheim, Springer, 2003.
- 5 V. N. Emel'yanenko, S. P. Verevkin and A. Heintz, *J. Am. Chem. Soc.*, 2007, **129**, 3930–3937.
- 6 S. P. Verevkin, Dz. H. Zaitsau, V. N. Emel'yanenko and A. Heintz, *J. Phys. Chem. B*, 2011, **115**, 12889–12895.
- 7 Dz. H. Zaitsau, G. J. Kabo, A. A. Strechan, Y. U. Paulechka, Y. U., A. Tschersich, S. P. Verevkin and A. Heintz, *J. Phys. Chem. A*, 2006, **110**, 7303–7306.
- 8 Dz. H. Zaitsau, V. N. Emel'yanenko, S. P. Verevkin and A. Heintz, *J. Chem. Eng. Data*, 2010, **55**, 5896–5899.
- 9 S. P. Verevkin, Dz. H. Zaitsau, V. N. Emel'yanenko, Y. U. Paulechka, A. V. Blokhin, A. B. Bazyleva and G. J. Kabo, *J. Phys. Chem. B*, 2011, **115**, 4404–4411.
- 10 G. Stridh and S. Sunner, *J. Chem. Thermodyn.*, 1975, **7**, 161–168.
- 11 E. A. Turner, C. C. Pye and R. D. Singer, *J. Phys. Chem. A*, 2003, **107**, 2277.
- 12 L. Glasser and H. D. B. Jenkins, *J. Chem. Eng. Data*, 2011, **56**, 874.
- 13 L. Glasser and H. D. B. Jenkins, *J. Am. Chem. Soc.*, 2000, **122**, 632.
- 14 J. Slattery, C. Daguene, P. Dyson, I. Krossing, H. Weingärtner and A. Oleinikova, *J. Am. Chem. Soc.*, 2008, **128**, 13427–13434.
- 15 L. Glasser and L. von Szentpály, *J. Am. Chem. Soc.*, 2006, **128**, 12314.
- 16 H. D. B. Jenkins, H. K. Roobottom, J. Passmore and L. Glasser, *Inorg. Chem.*, 1999, **38**, 3609–3620.
- 17 L. He, G.-H. Tao, D. A. Parrish and J. M. Shreeve, *Chem.–Eur. J.*, 2010, **16**, 5736–5743.
- 18 K. E. Gutowski, R. D. Rogers and D. A. Dixon, *J. Phys. Chem. B*, 2007, **111**, 4788–4800.
- 19 S. P. Verevkin, V. N. Emel'yanenko, Dz. H. Zaitsau, A. Heintz, Ch. D. Muzny and M. L. Frenkel, *Phys. Chem. Phys.*, 2010, **12**, 14994.
- 20 S. P. Verevkin, V. N. Emel'yanenko, A. A. Pimerzin and E. E. Vishnevskaya, *J. Phys. Chem. A*, 2011, **115**, 1992–2004.
- 21 S. P. Verevkin, R. V. Ralys, Dz. H. Zaitsau, V. N. Emel'yanenko and C. Schick, *Thermochim. Acta*, 2012, in press.
- 22 M. S. Kelkar and E. J. Maginn, *J. Phys. Chem. B*, 2007, **111**, 9424.