



Heat capacities of ionic liquids based on tetrahydrothiophenium cation and NTf₂ anion



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ARTICLE INFO

Keywords:

Ionic liquid
Heat capacity
Differential scanning calorimetry
Chain length dependence

ABSTRACT

The isobaric heat capacities of seven ionic liquids (ILs) based on the S-alkyl-tetrahydrothiophenium cation [C_nTHT]⁺ with alkyl chain lengths of C_n = 4,5,6,7,8,9,10 and the bis[(trifluoromethyl)sulfonyl]imide, [NTf₂]⁻ anion were measured in a differential scanning calorimeter in the temperature range 310–376 K. Measurements have been performed for the first time. Experimental results were extrapolated to the reference temperature of 298 K. A linear trend of the C_{p,m}^o(liq, 298 K) -values for [C_nTHT][NTf₂] with the growing alkyl chain length was observed and compared with trends available for the other ILs with 5-membered (imidazolium and pyrrolidinium) and 6-membered (pyridinium) ring cations as [NTf₂]⁻ salts. The new C_{p,m}^o(liq, 298 K) -values for [C_nTHT][NTf₂] were used for mutual validation of experimental and theoretical results by a group-additivity method available in the literature. The agreement observed between experimental and additive calculations, together with the reasonable chain-length dependence demonstrated for the [C_nTHT][NTf₂] series was considered as evidence of internal consistency of the heat capacities measured in this work.

1. Introduction

Ionic liquids (ILs) are considered as candidates for replacements of volatile solvents and heat-transfer liquids used in industry. For these applications, it is important to know their thermophysical and thermochemical properties. The ionic liquids bearing the bis[(trifluoromethyl)sulfonyl]imide (or NTf₂) anion combined with imidazolium [1], pyridinium [2], pyrrolidinium [3], and phosphonium [4] cations were studied in our laboratory, recently. ILs with the tetrahydrothiophenium cation (see Fig. 1) have attracted our attention due to their hydrophobic nature and their wide electrochemical window resulting in possible applications like dye-sensitized solar cells [5] or electric double-layer capacitors [6].

This paper extends our previous studies on the ILs containing fluorinated anions [1–4,7–9] and deals with heat capacity measurements on tetrahydrothiophenium based ILs with the [NTf₂]⁻ anion (see Fig. 1).

2. Experimental section

2.1. Materials

The samples of [C_nTHT][NTf₂] were prepared according to

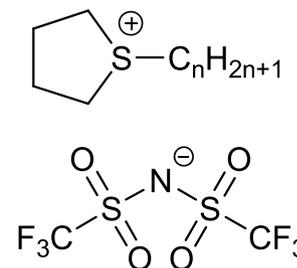


Fig. 1. S-alkyl-tetrahydrothiophenium based ILs [C_nTHT][NTf₂] with anion bis[(trifluoromethyl)sulfonyl]imide or NTf₂ = N(SO₂CF₃)₂ studied in this work: n = 4,5,6,7,8,9,10.

literature procedures based on the synthesis of Paulsson et al. [10]. Purities of ILs are given in Table S1. They were measured by using ion chromatography. Detailed description of synthesis, purification, and analytics will be published in a forthcoming paper. Before beginning the heat capacity measurements, the IL samples were kept at 333 K and 10⁻⁵ Pa for 1 h to remove possible traces of moisture and residual

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solvents. The negligible amount of residual moisture at the level of 10–20 ppm was confirmed by using Karl Fisher titration.

2.2. Heat capacity measurements

Isobaric heat capacities of liquid samples of $[C_n\text{THT}][\text{NTf}_2]$ ionic liquids were determined by using of a heat-compensation technique in Perkin Elmer Pyrus DSC 1 over the temperature range from 310 K–376 K. The temperature calibration of DSC was conducted with highly pure (> 99.9 mas %) reference materials indium, tin and lead. Temperature was measured with the standard uncertainty of 0.2 K. Standard calorimetric pans and samples (around 10–15 mg) were weighted with a Sartorius MSE3.6P-000-DM microbalance with the standard uncertainty of $5 \cdot 10^{-6}$ g.

The heat capacity measurements were carried in three steps. The first thermal scan was performed for an empty pan. In the second thermal scan the reference material (sapphire) was measured. The third run was carried out with the sample of ionic liquid.

According to elaborated by Perkin Elmer procedure, the whole temperature range of the typical DSC run was split in intervals of 50 K. The thermal profile of each interval started with 2 min isothermal step followed with temperature rise of 50 K (with heating rate of $10 \text{ K} \cdot \text{min}^{-1}$) and finished with the isothermal step of 2 min period at final temperature. The whole measuring profile was repeated 4 times and the results were averaged. The heat capacity was evaluated with the Perkin Elmer software.

The procedure of the heat capacity determination was tested with measurements on the reference sample of benzoic acid. Agreement our experimental results on the benzoic acid with those recommended in the literature [11] was within 1 %. The expanded uncertainty ($k = 2$) for the heat capacity measured by this method for ILs was estimated to be $0.02 \cdot C_{p,m}^{\circ}(\text{liq})$.

3. Results and discussion

3.1. Heat capacities as a function of temperature

Primary experimental data on heat capacities of ILs measured in the range 310 K–376 K are given in Table S2. For all ILs under study, the relationship between isobaric heat capacity and temperature was found to be approximately linear (see Fig. 2), with only about $55\text{--}65 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ increase observed over the temperature range used.

The experimental heat capacities temperature dependences were approximated with help of the linear equation:

$$C_{p,m}^{\circ}(\text{liq})/\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = A_0 + A_1 \cdot (T/\text{K}) \quad (1)$$

Coefficients of Eq. (1) as well as heat capacities $C_{p,m}^{\circ}(\text{liq}, 298 \text{ K})$ extrapolated to the reference temperature are collected in Table 1.

There are two heat capacity values for $[C_n\text{THT}][\text{NTf}_2]$ series available in the literature [5]: $C_{p,m}^{\circ}(\text{cr}, 298 \text{ K}) = 687 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ for $[C_2\text{THT}][\text{NTf}_2]$ and $C_{p,m}^{\circ}(\text{liq}, 283 \text{ K}) = 680 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ for $[C_4\text{THT}][\text{NTf}_2]$. The latter value is in significant disagreement with our result $C_{p,m}^{\circ}(\text{liq}, 298 \text{ K}) = 596 \pm 12 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ for $[C_4\text{THT}][\text{NTf}_2]$ (see Table 1, column 5). Insufficient details on DSC runs description given by Zhang et al. [5] make understanding of the reason for this difference difficult. However, it is apparent the internal inconsistency of heat capacities measured by Zhang et al. [5]. Indeed, according to the common sense, the heat capacity of $C_{p,m}^{\circ}(\text{cr}, 298 \text{ K})$ of $[C_2\text{THT}][\text{NTf}_2]$ reported by Zhang et al. [5] is expected to be lower in comparison to those of $C_{p,m}^{\circ}(\text{liq}, 283 \text{ K})$ for $[C_4\text{THT}][\text{NTf}_2]$, because the alkyl chain shorter and because the heat capacities of solid are generally lower in comparison to heat capacities of liquids. A monotonic increase of $C_{p,m}^{\circ}(\text{liq}, 298 \text{ K})$ in the homologous series $[C_n\text{THT}][\text{NTf}_2]$ could be considered as a proof of consistency experimental data measured in the current study.

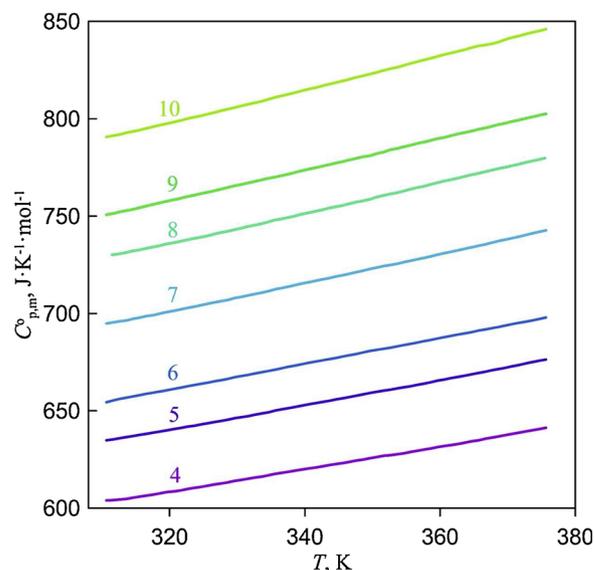


Fig. 2. Isobaric heat capacities of $[C_n\text{THT}][\text{NTf}_2]$ (with $n = 4, 5, 6, 7, 8, 9,$ and 10) as a function of temperature.

3.2. Chain length dependence of isobaric heat capacities

A monotonic increase of any property in a homologous series with the growing chain length is well-established phenomena. This behavior is common for molecular as well as for ionic compounds [1]. For example, the isobaric molar heat capacity in a homologous series of n-alkanes increases with the number of carbon atoms n in the alkyl chain according to Eq. (2) [12]:

$$C_{p,m}^{\circ}(\text{liq}, 298 \text{ K})/\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = (29.7 \pm 0.4) \times n + (17.2 \pm 3.8) \text{ with } R^2 = 0.999 \text{ for } \text{CH}_3 - (\text{CH}_2)_n - \text{CH}_3 \quad (2)$$

Also, in the homologous series of imidazolium based ILs with the $[\text{NTf}_2]$ anion, the increase with the growing alkyl chain is expressed according to Eq. (3) [1]:

$$C_{p,m}^{\circ}(\text{liq}, 298 \text{ K})/\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = (31.3 \pm 0.2) \times n + (442.4 \pm 1.8) \text{ with } R^2 = 0.999 \text{ for } [C_n\text{mim}][\text{NTf}_2] \quad (3)$$

It is apparent from comparison of two latter equations that slopes (or the contribution for the addition of the $-\text{CH}_2-$ fragment) are not much different for the molecular and ionic compounds. At the same time the intercepts of two latter equations are enormous dissimilar. The intercept represents the residual contribution to the total $C_{p,m}^{\circ}(\text{liq}, 298 \text{ K})$ -value of a homologue if n is extrapolated to zero. In the case of an IL it should be the “naked” cation with the completely cutted alkyl chain. The imidazolium, pyrrolidinium, and tetrahydrothiophenium cations are all 5-membered rings of comparable size. It is interesting to compare the “naked” contributions to the total $C_{p,m}^{\circ}(\text{liq}, 298 \text{ K})$ -values from the differently shaped 5-membered rings of imidazolium, pyrrolidinium, and tetrahydrothiophenium cations.

The heat capacity chain length dependence for the homologous series of pyrrolidinium-based ILs with the $[\text{NTf}_2]$ anion, is expressed according to Eq. (4) [3]:

$$C_{p,m}^{\circ}(\text{liq}, 298 \text{ K})/\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = (32.0 \pm 0.6) \times n + (460.6 \pm 4.4) \text{ with } R^2 = 0.999 \text{ for } [C_n\text{C1Pyr}][\text{NTf}_2] \quad (4)$$

The heat capacity chain length dependence for the homologous series of tetrahydrothiophenium based ILs with the $[\text{NTf}_2]$ anion (see Fig. 3) was derived using new experimental heat capacities derived in this work (see Table 1):

Table 1
Heat capacities of ionic liquids as a function of temperature at 0.1 MPa and coefficients of Eq. (1).

Compound	Trange, K	A_0 , ^a J·K ⁻¹ ·mol ⁻¹	A_1 , ^a J·mol ⁻¹	$C_{p,m}^o$ (liq, 298 K), ^b J·K ⁻¹ ·mol ⁻¹
[C ₄ THT][NTf ₂]	310 - 376	425.1 ± 2.3	0.5731 ± 0.007	596 ± 12
[C ₅ THT][NTf ₂]	310 - 376	440.5 ± 2.0	0.6241 ± 0.006	627 ± 13
[C ₆ THT][NTf ₂]	310 - 376	448.2 ± 1.2	0.6644 ± 0.004	646 ± 13
[C ₇ THT][NTf ₂]	310 - 376	470.1 ± 2.1	0.7217 ± 0.006	685 ± 14
[C ₈ THT][NTf ₂]	311 - 376	493.6 ± 2.1	0.7575 ± 0.007	719 ± 14
[C ₉ THT][NTf ₂]	310 - 376	506.7 ± 0.8	0.7851 ± 0.002	741 ± 15
[C ₁₀ THT][NTf ₂]	310 - 376	531.8 ± 2.0	0.8317 ± 0.006	780 ± 16

^a The expanded uncertainty with $k = 2$ and 0.95 confidence level is used.

^b The expanded uncertainty of $0.02 \times C_{p,m}^o$ (liq) was assigned after the test experiments with the reference sample of benzoic acid.

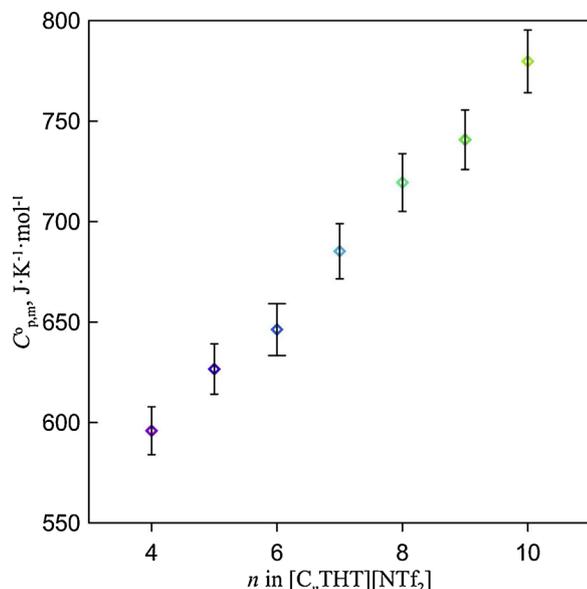


Fig. 3. Isobaric heat capacities of [C_nTHT][NTf₂] as a function of the chain length with $n = 4, 5, 6, 7, 8, 9$, and 10.

$$C_{p,m}^o(\text{liq}, 298 \text{ K})/J \cdot K^{-1} \cdot \text{mol}^{-1} = (30.5 \pm 2.0) \times n + (472 \pm 14) \text{ with } R^2 = 0.995 \text{ for } [C_n\text{THT}][\text{NTf}_2] \quad (5)$$

It is apparent from comparison of intercepts of Eqs. (4) and (5) that contributions for saturated 5-membered cycles with N- (460.6 ± 4.4 J·K⁻¹·mol⁻¹) and S-elements (472 ± 14 J·K⁻¹·mol⁻¹) are practically indistinguishable within their combined experimental uncertainties of 12–16 J·K⁻¹·mol⁻¹. However, the intercept of the quasi-aromatic 5-membered ring in imidazolium cation (440.5 J·K⁻¹·mol⁻¹) is somewhat lower in comparison to the saturated cycles, but the difference could be considered still as marginal within the aforementioned experimental uncertainties.

Ionic liquids based on the 6-membered ring cations (e.g. pyridinium, piperidinium, morpholinium, etc.) are also broadly discussed in the literature. Is the intercept (observed for the chain-length dependence) for 6-membered rings much different from those for 5-membered rings? The heat capacity chain length dependence for the homologous series of pyridinium based ILs with the [NTf₂] anion is expressed by Eq. (6) [2]:

$$C_{p,m}^o(\text{liq}, 298 \text{ K})/J \cdot K^{-1} \cdot \text{mol}^{-1} = (32.0 \pm 0.2) \times n + (454.0 \pm 2.0) \text{ with } R^2 = 0.999 \text{ for } [C_n\text{Py}][\text{NTf}_2] \quad (6)$$

The experimental $C_{p,m}^o$ (liq, 298 K) -data used to develop Eqs. (2–6) are compiled in Table S3. Uncertainties of coefficients of Eqs. (2–6) are expressed as expanded uncertainties with $k = 2$ and 0.95 confidence level.

To our surprise, the intercept even for the 6-membered ring (454.0 ± 2.0 J·K⁻¹·mol⁻¹) is indistinguishable (again within

combined experimental uncertainties of 12–16 J·K⁻¹·mol⁻¹) from heat capacity contributions of the “naked” 5-membered cations (between 442 and 472 J·K⁻¹·mol⁻¹). The comparison of coefficients of Eqs. (3–6) reveals that the type and size of cation hardly impacts the amount of the total $C_{p,m}^o$ (liq, 298 K) -value in the ILs containing [NTf₂] anion. Moreover, the slopes of Eqs. (3–6) are also very close (variations are between 30.5 to 32.0 J·K⁻¹·mol⁻¹). These two observations open a simple way for a quick assessment of $C_{p,m}^o$ (liq, 298 K) -values for ILs containing [NTf₂] anion and different types of alkyl substituted 5- and 6-membered rings. We have derived the weighted average values of slopes as well as of intercepts given in Eqs. (3–6) (uncertainties were taken as the weighing factor), and the general equation:

$$C_{p,m}^o(\text{liq}, 298 \text{ K})/J \cdot K^{-1} \cdot \text{mol}^{-1} = (31.7 \pm 0.2) \times n + (448.9 \pm 1.3) \text{ for } [\text{Cation}][\text{NTf}_2] \text{ with } (R^2 = 0.999) \quad (7)$$

can be used for a quick but trusty appraisal of the level of heat capacities of new ILs, where experiential data are absent yet. In order to test this approach, we used reliable experimental value [13] $C_{p,m}^o$ (liq, 298 K) = 607.5 ± 0.8 J·K⁻¹·mol⁻¹ for 1-butyl-1-methylpiperidinium bis[(trifluoromethyl)sulfonyl]imide ([C₄C₁pip][NTf₂]). Calculation according to Eq. 7 with $n = 5$ provides result $C_{p,m}^o$ (liq, 298 K) = 607 ± 10 J·K⁻¹·mol⁻¹ in good agreement with the experiment. However, we anticipate that the tetra-alkyl-ammonium and tetra-alkyl-phosphonium ILs do not obey Eq. 7 specified for the ring-shaped cations due two significantly different degree of branching of these cations. For the latter types of cations another specific chain length dependence should be developed.

3.3. Validation of group-contribution method for estimation of heat capacities $C_{p,m}^o$ (liq, 298 K)

In spite of a priory prevalence of experimental data over different kinds of estimates, the consistency of new experimental data with data already available in the literature is always required. One of the most broadly used methods to establish consistency of new results is a group-additivity (GA) method. In our recent study of [C_nmim][FAP] (with [FAP] = tris(pentafluoroethyl)trifluorophosphate) homologous IL series we arbitrary selected the most simple and straightforward additive approach based on an empirical formula for assessment of $C_{p,m}^o$ (liq, 298 K) developed by Ahamadi et al. [14]. The empirical formula and contributions for constituent elements are collected in Table S4. It has turned out that $C_{p,m}^o$ (liq, 298 K)-estimates for the series [C_nmim][FAP] were in good agreement with the available experimental data. This agreement has motivated application of the GA method by Ahamadi et al. [14] for the series of the S-alkyl-tetrahydrothiophenium ionic liquids [C_nTHT][NTf₂]. Results of $C_{p,m}^o$ (liq, 298 K) estimations are collected in Table 2, column 3.

As it can be seen from this table, the GA results are in agreement with our experiment, at least within the uncertainties ascribed to the $C_{p,m}^o$ (liq, 298 K) values listed in Table 1.

The agreement observed between experimental and GA results,

Table 2

Compilation of data on molar heat capacities $C_{p,m}^o$ and heat capacity differences (in $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$) at 298 K.

	$C_{p,m}^o(\text{liq})^a$	$C_{p,m}^o(\text{liq})^b$	(exp-calc)
[C ₄ THT][NTf ₂]	596 ± 12	583	13
[C ₅ THT][NTf ₂]	627 ± 13	614	13
[C ₆ THT][NTf ₂]	646 ± 13	646	0
[C ₇ THT][NTf ₂]	685 ± 14	679	6
[C ₈ THT][NTf ₂]	719 ± 14	711	8
[C ₉ THT][NTf ₂]	741 ± 15	744	-3
[C ₁₀ THT][NTf ₂]	780 ± 16	776	4

^a Experimental results from Table 1.

^b Calculated according to the group-additivity procedure suggested by Ahamadi et al. [4].

together with the reasonable chain-length dependence revealed for the [C_nTHT][NTf₂] series (see Section 3.2) can be considered as an evidence of internal consistency of the $C_{p,m}^o(\text{liq}, 298\text{ K})$ values measured in this work. These consistent results will be applied in the forthcoming paper for temperature adjustments of experimental vaporisation enthalpies measured with help of quartz-crystal microbalance for the [C_nTHT][NTf₂] series.

CRediT authorship contribution statement

Dmitry H. Zaitsau: Investigation, Validation, Formal analysis, Writing - review & editing. **Alexa Schmitz:** Investigation, Writing - review & editing. **Christoph Janiak:** Conceptualization, Methodology, Writing - original draft, Supervision. **Sergey P. Verevkin:** Conceptualization, Methodology, Writing - original draft, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work has been supported by the German Science Foundation (DFG) in the frame of the priority program SPP 1807 “Control of London Dispersion Interactions in Molecular Chemistry”, as well as of the priority program SPP 1708 “Material Synthesis Near Room Temperature” (grants VE 265-14/1 to SPV and JA 466/31-2 to C.J.). DHZ acknowledges the financial support from DFG, grant ZA 872/3-1, 407078203. This work

has been also partly supported by the Russian Government Program of Competitive Growth of Kazan Federal University and Russian Foundation for Basic Research No. 15-03-07475.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.tca.2020.178547>.

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