

Heat capacities of thiourea and some *N*-alkylthioureas

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Abstract

The molar heat capacities at constant pressure of thiourea (TU), 1-methyl-2-thiourea (MMTU), 1-ethyl-2-thiourea (METU), 1,3-diethyl-thiourea (DETU) and 1,1,3,3-tetramethyl-2-thiourea (TMTU) were determined by differential scanning calorimetry (DSC) from 310 K to about (10 to 30) K below their melting points. Values at 298.15 K were obtained by extrapolating the smoothed fitting equations as a function of temperature. For 1,3-dimethyl-2-thiourea (DMTU), measurements at around room temperature were used for direct determination of the $C_{p,m}$ experimental value at 298.15 K.

$C_{p,m}$'s at 298.15 K of all compounds increased linearly with the number of carbon atoms in the alkyl substituents. The contribution of $(25.5 \pm 1.5) \text{ J K}^{-1} \text{ mol}^{-1}$ per $-\text{CH}_2-$ group was in good accordance with the values previously obtained for some series of small peptides. The molar heat capacities of isomeric METU and DMTU were almost identical, whereas those of isomeric DETU and TMTU displayed an appreciable divergence. © 1997 Elsevier Science B.V.

Keywords: Thiourea; *N*-alkylthioureas; Heat capacity; DSC

1. Introduction

Heat capacities of pure substances are employed in many thermodynamic calculations, ranging from thermochemistry to solution chemistry, biochemistry and biophysics. $C_{p,m}$'s of pure solutes, in particular, are used to derive enthalpies of vaporisation and sublimation at 298.15 K from measurements at different temperatures, and hence obtain standard enthalpies of solvation as well as partial molar heat capacities of solutes at infinite dilution [1].

Thiourea and its *N*-alkyl derivatives are of great interest in several branches of chemistry. They are also employed as model compounds for studies in solution, especially with respect to their influence on the structure of water [2–6]. However, only an adiabatic calorimetry C_p value for thiourea [7] and an estimated C_p value for 1,1,3,3-tetramethyl-2-thiourea [8] have been reported.

This work is part of our studies on the thermodynamic properties of pure organic compounds, in some cases including their molar heat capacities at constant pressure [9–21]. Measurements were made by DSC from room temperature to below the melting points. We determined $C_{p,m} = f(T)$ relations for thiourea (TU), 1-methyl-2-thiourea (MMTU), 1-ethyl-2-

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thiourea (METU), 1,3-diethyl-2-thiourea (DETU) and 1,1,3,3-tetramethyl-2-thiourea (TMTU) and the corresponding extrapolated values at 298.15 K. For 1,3-dimethyl-2-thiourea (DMTU), the $C_{p,m}$ value at 298.15 K was directly determined.

2. Experimental

2.1. Materials

Thiourea and the *N*-alkylthioureas were analytical grade products from Aldrich and in part from Fluka. They were purified by repeated crystallizations from absolute ethanol or water–ethanol mixtures, dried under vacuum to constant mass at room temperature and kept in a desiccator until use. The purification of TMTU also included its sublimation under vacuum. Infrared spectroscopy determinations ruled out the presence of water traces in all compounds. The final purity of the samples was checked by the DSC peak-profile method and was always better than 99.8%. The purification procedures significantly increased their commercial purity despite the well-known difficulty of purifying this class of compounds, but did not provide the very good values previously obtained, e.g. for *N*-alkylureas [18]. Samples from both suppliers were used indifferently, since their origin did not appreciably affect the experimental results. The compounds examined are listed with their symbols, molar mass, origin and temperature of fusion after purification in Table 1.

Indium (NIST-RM 8758), benzoic acid (NPL-SRM M16-06, 99.99% mole fraction), urea (NIST-SRM 2152) and DL-alanine (Sigma DL-amino acids stan-

dard kit, 99% in weight) were used without further purification as reference materials.

2.2. Differential scanning calorimetry

A Mettler DSC 20 equipment coupled with a Mettler TC 10 A processor was employed. The manufacturer's temperature and heat calibration procedures were followed and the supplied special crucible containing very high-purity In, Pb and Zn was used [22]. The built-in programme for determining the actual sample temperatures at various scanning rates is based on the melting points of these three metals (429.75, 600.55, 692.65 K, respectively), whose values are incorporated. The heat-flux detector was calibrated by another built-in programme based on the heat of fusion of In ($3.266 \text{ kJ mol}^{-1}$) also incorporated. All these temperature and heat-of-fusion values are in very good agreement with those reported in updated papers on DSC calibration [23,24] and recommended by ASTM [25]. A check with at least five melting runs with indium from NIST showed an agreement with the reference values within 0.02% for temperature and 0.2% for enthalpy. The calibration and experimental procedures employed for our Mettler DSC 20 equipment are described in detail in Ref. [17].

2.3. Heat capacity measurements

The experimental conditions were selected after a preliminary study [26]: sample pellets of about 30 mg in sealed aluminium crucibles and a heating rate of 10 K min^{-1} in static air were used. The procedure was calibrated with benzoic acid, a recommended reference material for solid organic samples [27]. For the sake of consistency, reference was made to only one

Table 1
Thiourea and *N*-alkylthioureas, with their symbols, molar mass, commercial origin and temperature of fusion

Compound	$M/\text{g mol}^{-1}$ ^a	Origin	T_{fus}/K ^b
Thiourea (TU)	76.122	Aldrich	444.7 ± 0.5
1-methyl-2-thiourea (MMTU)	90.149	Aldrich, Fluka	392.4 ± 0.1
1-ethyl-2-thiourea (METU)	104.176	Aldrich	380.8 ± 0.4
1,3-dimethyl-2-thiourea (DMTU)	104.176	Aldrich	336.9 ± 0.5
1,3-diethyl-2-thiourea (DETU)	132.230	Aldrich, Fluka	350.0 ± 0.2
1,1,3,3-tetramethyl-2-thiourea (TMTU)	132.230	Aldrich, Fluka	350.4 ± 0.1

^a Based on the 1991 IUPAC table of standard atomic weights of the elements.

^b Temperature of fusion after purification.

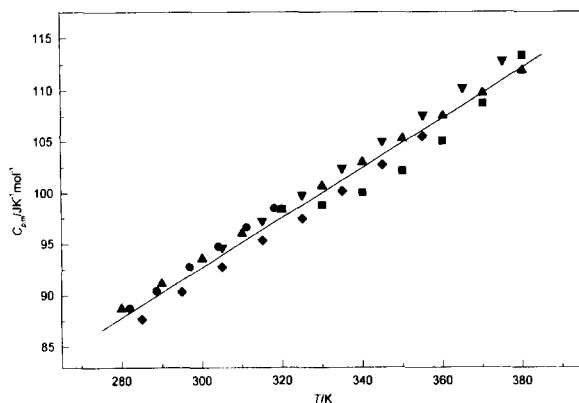


Fig. 1. Molar heat capacity of urea as a function of temperature in the range (280 to 380) K: (—), smoothing equation, present work; ◆, Ferloni and Della Gatta. [18]; ▼, Gambino and Bros [30]; ▲, Kozyro et al. [31]; ●, Ruehrwein and Huffman [32]; ■, Vogel and Schuberth [33].

set of experimental data by Arvidsson et al. [28]. A number of runs from room temperature to about 370 K were carried out and $C_{p,m}$ values for each run were determined in 5 K intervals through the built-in heat-capacity measurement programme [22,29]. Averaged heat capacity values of benzoic acid at various temperatures fell within 1.5% uncertainty range and were linearly smoothed. This gave rise to a $C_{p,m}$ at 298.15 K of $145.97 \text{ J K}^{-1} \text{ mol}^{-1}$, in good agreement with the reference value of $146.79 \text{ J K}^{-1} \text{ mol}^{-1}$ [28]. Moreover, a suitable conversion factor was calculated to fully superimpose our smoothed curve on that of the reference.

The correctness of our full experimental procedure was checked by determining the heat capacities of urea and DL-alanine from room temperature to about 380 K.

For urea, our experimental data generated the smoothed equation $C_{p,m}/(\text{J K}^{-1} \text{ mol}^{-1}) = (19.52 \pm 1.31) + (0.244 \pm 0.007)(T/\text{K})$, which corresponds to a satisfactory average of a comprehensive number of literature data [18,30–33], as shown in Fig. 1.

For DL-alanine, the equation $C_{p,m}/(\text{J K}^{-1} \text{ mol}^{-1}) = (3.85 \pm 4.32) + (0.392 \pm 0.013)(T/\text{K})$ led to the value $C_{p,m}(298.15 \text{ K}) = (120.55 \pm 0.62) \text{ J K}^{-1} \text{ mol}^{-1}$ in good agreement with that extrapolated from the data in the interval (200 to 298) K from the only reported set of experimental measurements, i.e. $(121.99 \pm 0.06) \text{ J K}^{-1} \text{ mol}^{-1}$ [34].

The experimental measurements were performed from room temperature to about (10 to 30) K below the melting points of the samples, with the same conditions as in the calibration runs. A minimum of 5 scans were made for each compound. Data were taken in 5 K intervals, starting from 313 K because of the time needed for the calorimetric base line to reach stability. Since DETU and TMTU melt at about 350 K, their data were taken in only 2 K intervals, starting from 310 K. For DMTU, determinations with our calorimeter could not be considered fully reliable because of its lower fusion temperature (336.9 K), which led to an insufficiently wide measurement interval. Some runs were therefore made at around ambient temperature at the Pabisch–Mettler laboratories in Milan, Italy, with a DSC 30 calorimeter that can be used in the subambient temperature range.

3. Results and discussion

The experimental molar heat capacities of TU, MMTU and METU are reported in Table 2 and those of DETU and TMTU in Table 3. The relevant plots are presented in Fig. 2. In view of their linear trend as a function of temperature, the data were successfully smoothed by curves fitting the equation $C_{p,m}/(\text{J K}^{-1} \text{ mol}^{-1}) = A + B(T/\text{K} - 298.15 \text{ K})$. The

Table 2
Molar heat capacities $C_{p,m}/(\text{J K}^{-1} \text{ mol}^{-1})$ for TU, MMTU and METU at selected temperatures

T/K	TU	MMTU	METU
313	99.83	120.76	158.32
318	100.95	122.16	160.27
323	101.60	123.02	163.03
328	102.61	124.21	163.97
333	103.74	125.73	165.67
338	104.45	126.82	168.39
343	105.34	128.20	171.21
348	106.91	130.48	174.34
353	107.02	131.62	176.42
358	108.30	133.54	179.30
363	109.68	135.40	182.01
368	111.29	137.15	
373	112.19	138.52	
378	113.23	140.25	
383	114.54		
388	115.86		
393	116.82		

Table 3

Molar heat capacities $C_{p,m}/(\text{J K}^{-1} \text{mol}^{-1})$ for DETU and TMTU at selected temperatures

T/K	DETU	TMTU
310	207.41	197.05
312	208.35	197.77
314	209.33	198.80
316	210.27	199.93
318	211.39	200.70
320	212.25	201.92
322	212.98	202.81
324	215.02	202.91
326	215.94	204.56
328	216.06	205.93
330	217.61	206.86
332	218.65	206.87
334	219.17	208.27
336	220.56	210.38
338	221.46	210.45
340	221.99	211.61

intercepts (A), slopes (B) and correlation coefficients (r) for all the compounds are shown in Table 4 (Columns 4, 5 and 6, respectively), together with the experimental temperature ranges (Column 2). The intercepts (A) represent the heat capacities at 298.15 K, because there were no solid–solid transitions or other anomalies from ambient up to the temperature of the first experimental value. The heat capacity of DMTU at 298.15 K as averaged from four determinations at around room temperature is also reported in Table 4. Fig. 3 shows that the molar heat capacities at 298.15 K regularly increase with the

Table 4

Molar heat capacities as a function of temperature from the equation $C_{p,m}/(\text{J K}^{-1} \text{mol}^{-1}) = A + B(T/\text{K} - 298.15 \text{ K})$, where $A = C_{p,m}(298.15 \text{ K})$

Compound	T/K	N^a	A	B	r^b
TU	313–393	17	96.2 ± 0.2^c	0.213 ± 0.004	0.99723
MMTU	313–378	14	115.4 ± 0.4	0.305 ± 0.007	0.99668
METU	313–363	11	150.4 ± 0.7	0.475 ± 0.015	0.99543
DMTU			150.8 ± 0.7^d		
DETU	310–340	16	201.5 ± 0.2	0.500 ± 0.008	0.99799
TMTU	310–340	16	191.1 ± 0.3^e	0.489 ± 0.010	0.99664

Uncertainties are standard deviations.

^a Number of points used in the least-squares treatment.

^b Product-moment correlation coefficient.

^c [7], $96.9 \text{ J K}^{-1} \text{mol}^{-1}$.

^d Average of four determinations measured at Pabisch–Mettler (Milan, Italy).

^e [8], $160 \text{ J K}^{-1} \text{mol}^{-1}$, estimated value.

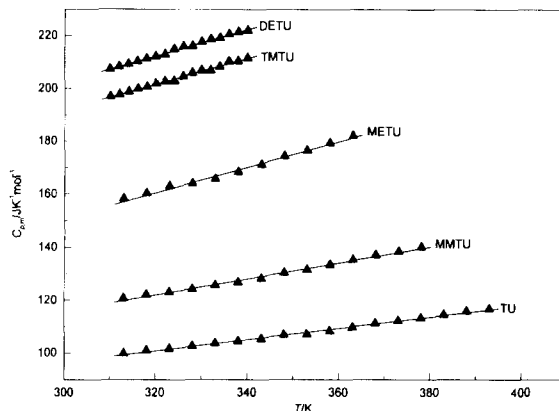


Fig. 2. Molar heat capacities of TU, MMTU, METU, DETU and TMTU as a function of temperature.

number of carbon atoms of the alkyl substituents, n_C , giving a $C_{p,m}$ increment of $(25.5 \pm 1.5) \text{ J K}^{-1} \text{mol}^{-1}$ per methylene group.

The results suggest the following observations.

1. Our heat capacity value for TU at 298.15 K, $(96.2 \pm 0.2) \text{ J K}^{-1} \text{mol}^{-1}$, is in very good agreement with the $96.9 \text{ J K}^{-1} \text{mol}^{-1}$ obtained by adiabatic calorimetry by Westrum and Chang [7] at the same temperature. No further comparisons with literature data are possible since no other heat capacity measurements have been undertaken on this class of compounds. The $C_{p,m}$ of $160 \text{ J K}^{-1} \text{mol}^{-1}$ reported for TMTU by Inagaki et al. is actually an estimated value [8].

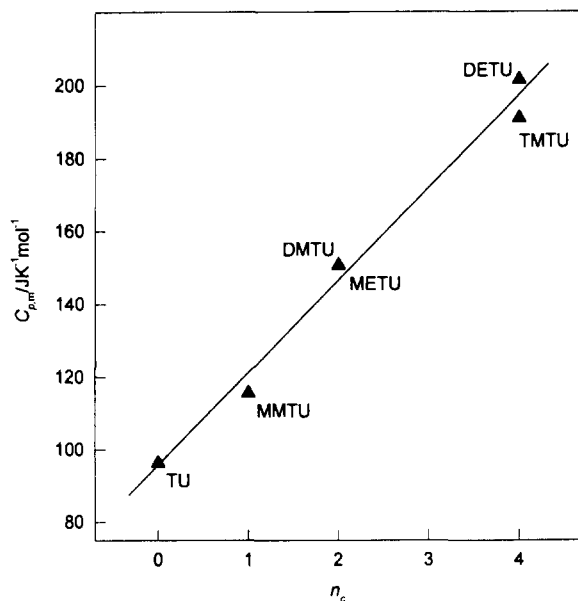


Fig. 3. Molar heat capacities at 298.15 K of TU, MMTU, METU, DMTU, DETU and TMTU as function of the number of carbon atoms, n_c , in their alkyl substituents.

- The $C_{p,m}$'s of isomeric METU and DMTU are very similar (150.4 and $150.8 \text{ J K}^{-1} \text{mol}^{-1}$, respectively), whereas the $C_{p,m}$ of TMTU ($191.1 \text{ J K}^{-1} \text{mol}^{-1}$) is lower by about 5% than that of its isomer DETU ($201.5 \text{ J K}^{-1} \text{mol}^{-1}$). The crystal structures of practically all the alkylthioureas are not yet known and so a discussion in terms of possible similarities or differences between these compounds is not possible. However, these findings agree with the closeness of the enthalpies of sublimation for DMTU and METU (110 and 120 kJ mol^{-1}) and their noticeable divergence for TMTU and DETU (84 and 121 kJ mol^{-1}), as from our results in course of publication [21].
- The heat capacity of the solid methylene group at 298.15 K ($25.5 \text{ J K}^{-1} \text{mol}^{-1}$) is in good agreement with our previous values at the same temperature for *N*-acetyl-*N*-methylamino acid amides ($25.1 \text{ J K}^{-1} \text{mol}^{-1}$) [17], and *N*-acetylamino acid amides and 2,5-diketopiperazines ($26.7 \text{ J K}^{-1} \text{mol}^{-1}$) [20]. A very similar value ($25.0 \text{ J K}^{-1} \text{mol}^{-1}$) can also be obtained from the smoothed $C_{p,m}$'s at 298.15 K for urea and a comprehensive group of 12 variously substituted

solid *N*-alkylureas reported by Kabo et al. [35]. By contrast, the value from our previous measurements on urea and four monosubstituted *N*-alkylureas [18] is higher, i.e. $31.5 \text{ J K}^{-1} \text{mol}^{-1}$. However, a similar discrepancy (though somewhat smaller) would also be observed for the data in Ref. [35], if only those for urea and our monosubstituted compounds were considered. The near-complete absence in the literature of crystal structures for *N*-alkylureas also prevents a suitable basis to comment on these findings. In any case, the presence of a typical H-bond network in urea and all *N*-alkylureas, except for tetraalkyl derivatives, by respect with *N*-alkylthioureas should be considered.

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