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Thermochimica Acta 441 (2006) 20–26
thermochimica acta
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Thermophysical properties of sulfur heterocycles: Thiane and thiophene derivatives

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Received 8 June 2005; received in revised form 7 November 2005; accepted 14 November 2005

Abstract

The present study reports a DSC study of the sulfur heterocyclic compounds: 2,2'-bithiophene [492-97-7]; 2,5-thiophenedicarboxylic acid [4282-31-9]; 3-acetylthiophene [1468-83-3]; 2-thiopheneacetic acid [1918-77-0]; 3-thiopheneacetic acid [6964-21-2]; 1,4-dithiane sulfone [139408-38-1]; 1,3-oxathiane-3,3-dioxide (1,3-oxathiane sulfone) [109577-03-9] and 1,4-oxathiane-4,4-dioxide (1,4-oxathiane sulfone) [107-61-9] in the temperature interval $T = 268$ K and the melting temperatures. Temperatures, enthalpies and entropies of fusion are reported. 1,4-Oxathiane sulfone presents solid–solid phase transitions near to fusion. No additional solid–solid phase transitions were observed for the other solid compounds. For the compounds that are solids over the temperature interval, the heat capacity of the condensed phase was measured. Heat capacities at $T = 298.15$ K for the liquids 2-acetylthiophene [88-15-3]; methyl, 2-thiopheneacetate [19432-68-9]; methyl, 3-thiopheneacetate [58414-52-1] and thiazole [288-47-1] were also measured. The $C_{p,\mathrm{m}}$ (298.15 K) values obtained in this work were compared with the available experimental data and with values estimated with group contribution schemes.

Keywords: DSC; Heat capacity; Fusion enthalpy; Thiophene derivatives; Thiane derivatives; Sulfur heterocyclic compound

1. Introduction

Despite the importance and applications of sulfur containing compounds, the thermochemical and thermophysical data existing in the literature are scarce [1], whereas the same values are available for many of the oxygen analogues. This work is part of a systematic study of thermochemical and thermophysical properties of sulfur heterocyclic compounds [2–13]. This work reports the temperature, enthalpy and entropy of fusion, and heat capacities of several thiophene and thiane derivatives measured by differential scanning calorimetry (DSC). The target compounds are 2,2'-bithiophene; 2,5-thiophenedicarboxylic acid; 2-acetylthiophene; 3-acetylthiophene; 2-thiopheneacetic acid; 3-thiopheneacetic acid; methyl, 2-thiopheneacetate; methyl, 3-thiopheneacetate; thiazole; 1,4-dithiane-1,1-dioxide (1,4-dithiane sulfone); 1,3-oxathiane-3,3-dioxide (1,3-oxathiane sulfone) and 1,4-oxathiane-4,4-dioxide (1,4-oxathiane sulfone).

Heat capacities at 298.15 K have proven quite useful in adjusting vaporization, sublimation and fusion enthalpies with temperature. Equations for doing this have recently been reported by Chickos and coworkers [14,15]. There are several compilations of critically evaluated calorimetrically measured heat capacities in the literature [16–18], but new data on heat capacity for important families of compounds are needed [19]. There has been an effort to develop reliable and accurate group contribution schemes to improve the estimation and compensate for the scarcity of this data. The simplest schemes are based on first order additivity and only consider the constituent atoms of the molecule. Other methods use a second order additivity that takes into account the nearest-neighbour interactions in the definition of structural units of molecules. These schemes normally neglect all next-to-nearest-neighbour interactions due to the limited accuracy of the available experimental heat capacity data, and because differences among values of structural isomers are as large as the uncertainty of the methods.

Several heat capacity estimation methodologies by group additivity have been reported [20,21]. The method of Růžička and Domalski [20] is based on the second order additivity

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0040-6031/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2005.11.024

scheme proposed by Benson et al. for ideal gases [22,23] and for liquid hydrocarbons [24] and yields the heat capacity of organic liquids as a function of temperature in an analytical form. The procedure by Chickos et al. [21] is only valid for $C_{p,\mathrm{m}}(T = 298.15\,\mathrm{K})$ estimations for both liquid and solid compounds and utilizes a simple first order additivity scheme. Very recently, with the availability of more experimental data, an update of previous work [20] has been reported by Zábranský and Růžička [25] amending the existing group contributions and developing new parameters to cover a larger number of groups and structural units. Some new and refined parameters for the first order additivity scheme [21] have also been reported [6,26].

The main problems with the estimation routines are: (1) some adjusted group contribution values are based only in a limited number of experimental data, as is the case of sulfones and sulfoxides; (2) fused ring, H-bond, cis, ortho, diaxial, etc. corrections are sometimes needed to improve the estimated value and some of these corrections are not very well established or are missing; (3) in the case of solid compounds, the existence of phase transitions or fusion that cannot be predicted gives a lower estimated heat capacity value in the temperature interval where this process takes place.

An objective of this work was to expand the database of available experimental heat capacities of sulfur heterocycles, and to provide reliable data to adjust and refine group contribution schemes for the estimation of this property.

2. Experimental

2.1. Materials

Thiophene derivatives were all obtained from commercial vendors in high chemical purity (98+%). 2- and 3-Thiopheneacetic acids were purified by crystallization twice from *n*-hexane and then from petroleum ether. 2,5-Thiophenedicarboxylic acid was crystallized twice from water. 3-Acetylthiophene was purified by crystallization twice from petroleum ether. To obtain dry and pure 2-acetylthiophene; methyl, 2- and 3-thiopheneacetates, and thiazole the liquid commercial compounds were dried over molecular sieves before distillation. This treatment was repeated three times for every compound.

1,4-Dithiane sulfone was synthesized following the procedure of Clennan et al. [27] using 1,4-dithiane sulfoxide as precursor. The sulfoxide was previously obtained according to the procedure described by Khan et al. [28]. In a round-bottom 1000-mL flask was placed 5.0 g (36.7 mmol) of 1,4-dithiane 1-oxide and 370 mL of water. The resulting solution was treated with 12.25 g of $MgSO_4$ dissolved in 360 mL of water, and then with 3.9 g (24.6 mmol) of $KMnO_4$ in 240 mL of water. The reaction mixture was stirred for 1.5 h, treated with 15 g (78.9 mmol) sodium metabisulfite to destroy the excess of oxidizing reagent. The resulting colorless mixture was filtered, extracted with CH_2Cl_2, and evaporated at reduced pressure. The crude product was purified by flash column chromatography (CH_2Cl_2-EtOAc, 4:1) to afford the expected sulfone (4.9 g, 88% yield).

The procedure described in the literature [29] was slightly modified to synthesize 1,3- and 1,4-oxathiane sulfone. In a round-bottom 100-mL flask was placed 0.9 mL (9.6 mmol) of 1,4-oxathiane or 1.0 g (9.6 mmol) of 1,3-oxathiane and 15 mL of acetic acid. The resulting solution was treated with 15 mL (0.49 mol) of hydrogen peroxide and the reaction mixture was stirred at ambient temperature for 2 days. The solvent was removed at reduced pressure and the solid residue was crystallized from CH_2Cl_2–hexane (2:8). In the case of 1,3-oxathiane sulfone, final purification was achieved by sublimation (110 °C/4 mmHg) to give the expected sulfone (1.0 g, 77% yield), mp 129–131 °C (lit. mp 128–130 °C). For 1,4-oxathiane sulfone: (0.9 g, 69% yield), mp 77–79 °C. ^1H NMR ($CDCl_3$, 300 MHz) δ 2.32–2.38 (m, 2H), 3.17–3.21 (m, 2H), 3.84–3.88 (t, 2H), 4.53 (s, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 25.5, 50.9, 68.5, 84.4. Anal. Calcd. for $C_4H_8O_3S$: C, 35.28; H, 5.92. Found: C, 34.92; H, 6.32.

All solid samples were carefully dried under vacuum at 50 °C. Determination of purities, assessed by g.c. and DSC by the fractional fusion technique [30,31] indicated that the mole fraction of impurities in all the compounds was less than 0.002.

The standards used for DSC calibration were hexafluorobenzene, 99.9 % purity, was supplied by Aldrich; benzoic acid was NIST standard reference sample 39j; and high-purity indium (mass fraction: >0.99999) and tin were supplied by Perkin-Elmer.

2.2. Calorimetry

A differential scanning calorimeter (Perkin-Elmer, Pyris 1) equipped with an intra-cooler unit was used to monitor purity, to study the fusion process, the possible existence of phase transitions in the solid samples, and to measure the heat capacity of all compounds. Temperature and power scales were calibrated [32–34] at heating rates of 0.04 and 0.17 K s^{-1}. The temperature scale was calibrated by the melting temperature of the high-purity reference materials: hexafluorobenzene, benzoic acid, tin and indium [35]. The power scale was calibrated with high-purity indium [35].

Thermograms of samples hermetically sealed in aluminium pans were recorded in a nitrogen atmosphere. All the pans with the samples were weighed on a Mettler AT21 microbalance with a detection limit of 1×10^{-6} g, before and after the experiments to confirm that no product had volatilized.

After calibration, several runs with high-purity benzoic acid and indium as reference materials [35] were performed under the same conditions as the experimental determinations. The results are given in Table 1. The uncertainties of the experimental temperatures and enthalpies of fusion are expressed as the standard deviation of the mean. The accuracies for the temperatures and enthalpies of fusion were calculated [36] as the percentage deviation of the experimental data with regard to the values given in the literature [35]. T_{fus} were taken as DSC onset temperatures.

For determination of purity and temperature and enthalpy of fusion, a heating rate of 0.04 K s^{-1} was used. For each solid compound, five to eight samples weighing 1–2 mg were recorded.

Table 1
Temperatures and enthalpies of fusion of reference compounds

Compound	N[a]	T_{fus} (K)			$\Delta_{fus}H$ (J mol^{-1} K^{-1})		
		This work	Literature [35]	D (T_{fus}, %)	This work	Literature [35]	D ($\Delta_{fus}H$, %)
Benzoic acid[b]	6	395.7 ± 0.1	395.50 ± 0.02	0.1	17.78 ± 0.13	18.063 ± 0.042	−1.6
Indium[c]	8	430.5 ± 0.1	429.75 ± 0.04	0.2	3.24 ± 0.10	3.286 ± 0.013	−1.3

[a] N denotes the number of DSC runs.
[b] NIST: (National Institute of Standards and Technology) standard reference sample 39j.
[c] Supplied by Perkin-Elmer.

Table 2
$C_{p,m}$ values of reference compounds

T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})		
	This work	Literature [35]	$D(C_{p,m}$,%)
α-Aluminum oxide			
298.15	78.7 ± 0.1	79.01	−0.4
300	79.2 ± 0.1	79.41	−0.3
350	88.5 ± 0.3	88.84	−0.4
400	95.4 ± 0.7	96.08	−0.7
Benzoic acid			
280	137.2 ± 0.6	138.44	−0.9
300	145.3 ± 0.7	147.64	−1.6
320	155.1 ± 0.7	156.87	−1.2
350	168.7 ± 0.8	170.70	−1.2

A fresh sample was used for each run. All solid compounds showed thermal stability in the fusion process.

Different scans were performed on heating, cooling and second heating, to determine the possible existence of phase transitions or polymorphism in the samples over the temperature range from $T = 268$ K to their respective melting temperature at heating rates of 0.04 and 0.17 K s^{-1}.

Heat capacities were determined by the “scanning method” following the experimental methodology previously described [36–38] with synthetic sapphire (α-aluminum oxide) as reference material [35–37]. To check the experimental method, heat capacity experiments were made with benzoic acid and synthetic sapphire as reference materials [35] in the temperature intervals $T = 268$–360 K, and $T = 268$–410 K, respectively. Table 2 gives the mean values for heat capacity determinations at the selected temperatures and their uncertainties expressed as the standard deviations of the mean. A comparison of our results with those reported in the literature [35] is also given.

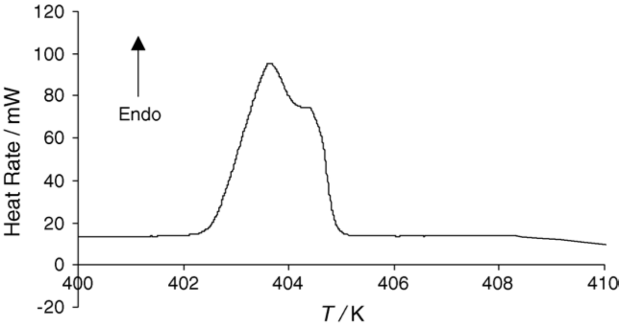

Fig. 1. Fusion detail of 1,4-oxathiane sulfone.

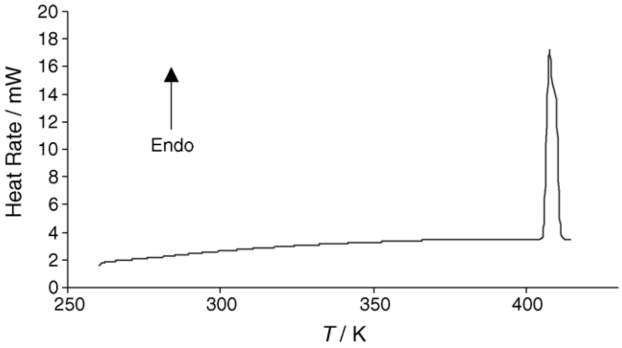

Fig. 2. First heating of 1,4-oxathiane sulfone.

The quantity $D(C_{p,m})$ defined as the relative percentage error gives the accuracy [36] of our measurements. The mass of sapphire used in each run was 0.030345 g. For heat capacity

Table 3
Temperatures and enthalpies of fusion for solid compounds

Compound	Purity (%)	T_{fus} (K)[a]	$\Delta_{fus}H$ (k J mol^{-1})	$\Delta_{fus}S$ (k J mol^{-1} K^{-1})
2,2’-Bithiophene	99.853 ± 0.003	304.2 ± 0.1	16.5 ± 0.1	54.2 ± 0.3
3-Acetylthiophene	99.953 ± 0.003	333.6 ± 0.1	18.9 ± 0.1	56.6 ± 0.4
2-Thiopheneacetic acid	99.913 ± 0.013	337.4 ± 0.1	14.0 ± 0.1	41.3 ± 0.2
3-Thiopheneacetic acid	99.917 ± 0.005	353.3 ± 0.1	18.8 ± 0.1	53.2 ± 0.1
1,4-Dithiane sulfone	99.965 ± 0.005	474.2 ± 0.1	26.0 ± 0.1	54.8 ± 0.2
1,3-Oxathiane sulfone	99.843 ± 0.006	352.9 ± 0.1	15.2 ± 0.1	43.0 ± 0.1
1,4-Oxathiane sulfone	99.920 ± 0.012	403.3 ± 0.2	20.2 ± 0.1[b]	50.1 ± 0.1[b]

[a] Taken as DSC onset temperatures.
[b] Total phase change enthalpy including the phase transitions not resolved in the fusion process.

Table 4
Experimental $C_{p,\mathrm{m}}$ values for some solid thiophene derivatives

T (K)	$C_{p,\mathrm{m}}$ (J K^{-1} mol^{-1})	T (K)	$C_{p,\mathrm{m}}$ (J K^{-1} mol^{-1})	T (K)	$C_{p,\mathrm{m}}$ (J K^{-1} mol^{-1})
2,2’-Bithiophene					
263.15	175.4	280.15	185.6	295.15	198.5
265.15	176.2	285.15	189.3	298.15	205.5
270.15	178.3	290.15	192.9	300.15	218.1
275.15	182.4	291.15	193.6		
3-Acetylthiophene					
268.15	134.0	280.15	138.7	295.15	145.0
270.15	134.9	285.15	140.3	298.15	146.1
275.15	136.7	290.15	142.4	300.15	147.5
2-Thiopheneacetic acid					
268.15	146.3	290.15	155.2	310.15	166.1
270.15	147.2	295.15	157.6	315.15	168.5
275.15	149.6	298.15	159.2	320.15	170.5
280.15	150.9	300.15	160.3	325.15	173.6
285.15	153.4	305.15	163.9		
3-Thiopheneacetic acid					
268.15	151.1	295.15	166.6	320.15	182.7
270.15	152.6	298.15	168.4	325.15	186.8
275.15	155.6	300.15	169.8	330.15	190.6
280.15	158.5	305.15	172.7	335.15	193.9
285.15	160.8	310.15	175.3	340.15	198.7
290.15	163.6	315.15	178.8		
2,5-Thiophenedicarboxylic acid					
277.15	161.4	330.15	178.1	390.15	200.9
280.15	162.7	335.15	179.7	395.15	203.3
285.15	163.7	340.15	180.8	400.15	206.1
290.15	164.7	345.15	182.3	405.15	209.6
295.15	166.4	350.15	184.0	410.15	210.9
298.15	167.1	355.15	186.1	415.15	213.7
300.15	167.7	360.15	186.4	420.15	216.3
305.15	169.5	365.15	190.1	425.15	219.4
310.15	171.0	370.15	192.4	430.15	223.1
315.15	173.1	375.15	194.2	435.15	225.5
320.15	175.1	380.15	196.7	440.15	228.1
325.15	177.0	385.15	198.7	445.15	229.8

determinations, four to six fresh samples weighing 10–25 mg were scanned for each solid compound in the temperature range from 268 K to its melting temperature at 0.17 K s^{-1}. The complete temperature ranges for determination of the heat capacities were divided in intervals of approximately 40 K, overlapping by 5 K from one interval to another. For liquid compounds, three to five determinations in the temperature interval 268–308 K, were made to obtain heat capacity values at $T = 298.15$ K. The estimated uncertainty of the molar heat capacities is less than 2%. The experimental results for the solid compounds were fit to a second order polynomial in temperature.

3. Experimental results

The purity, fusion temperatures and enthalpies and the calculated entropy of fusion of the solid compounds are given in Table 3. The uncertainty was taken as the standard deviation of the mean. 2,5-Thiophenedicarboxylic acid decomposes before melting and the fusion process could not be studied by DSC.

The only value in the NIST database [39] to compare with our results is the fusion temperature of 2,2’-bithiophene. The data reported, 306 K [40] and 304–306 K [41], are in fair agreement with our value.

1,4-Oxathiane sulfone showed a shoulder in the fusion peak not resolved by the calorimeter (Fig. 1). Scan rates from 0.04 to 0.83 K s^{-1} did not separate the peaks. Fig. 2 shows the first heating of the sample from $T = 268$ K to its melting point and does not show any phase transition prior to melting. Several phase transitions appear in a first cooling scan (Fig. 3). This behaviour was reproducible being observed in all the runs per-

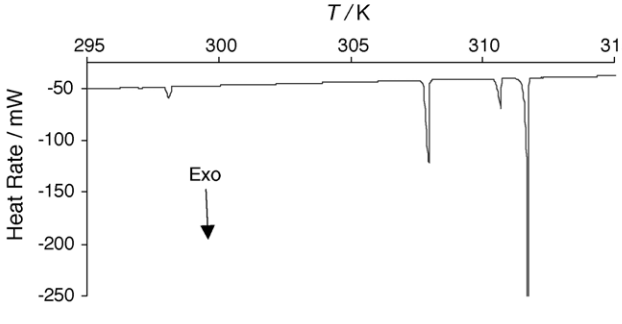

Fig. 3. First cooling of 1,4-oxathiane sulfone.

Table 5
Experimental $C_{p,\mathrm{m}}$ values for some solid thiane derivatives

T (K)	$C_{p,\mathrm{m}}$ (J K^{-1} mol^{-1})	T (K)	$C_{p,\mathrm{m}}$ (J K^{-1} mol^{-1})	T (K)	$C_{p,\mathrm{m}}$ (J K^{-1} mol^{-1})
1,4-Dithiane sulfone					
268.15	141.0	330.15	167.5	400.15	203.3
270.15	141.7	335.15	168.9	405.15	205.7
275.15	143.8	340.15	171.0	410.15	209.1
280.15	145.9	345.15	173.0	415.15	212.2
285.15	148.1	350.15	175.1	420.15	215.5
290.15	149.8	355.15	177.4	425.15	218.8
295.15	151.8	360.15	179.5	430.15	222.8
298.15	152.7	365.15	181.6	435.15	226.2
300.15	153.5	370.15	184.4	440.15	230.2
305.15	155.6	375.15	186.2	445.15	234.7
310.15	158.1	380.15	189.1	450.15	239.4
315.15	160.5	385.15	191.2	454.15	243.2
320.15	163.0	390.15	195.1		
325.15	165.5	395.15	199.6		
1,3-Oxathiane sulfone					
268.15	133.2	295.15	146.3	315.15	161.5
270.15	134.5	298.15	148.1	320.15	164.8
275.15	136.5	300.15	149.6	325.15	168.3
280.15	138.6	305.15	153.8	330.15	171.7
285.15	140.6	310.15	158.6	335.15	176.3
290.15	143.3				
1,4-Oxathiane sulfone					
268.15	134.2	305.15	151.2	350.15	172.8
270.15	135.4	310.15	153.1	355.15	175.5
275.15	137.3	315.15	155.3	360.15	177.7
280.15	139.3	320.15	157.6	365.15	180.1
285.15	141.7	325.15	159.9	370.15	182.5
290.15	144.2	330.15	162.0	375.15	185.6
295.15	146.6	335.15	164.1	380.15	188.6
298.15	147.9	340.15	166.9	385.15	191.5
300.15	148.9	345.15	170.3	390.15	194.7

formed. Reheating and cooling scans present similar behaviour showing the reversibility of the process. In the second cooling scan, a shift to higher temperature, about 20 K, in the crystallization process was obtained. After storage in a desiccator for several months, new runs were made; the phase transitions did not disappear but the relative intensities of the peaks changed.

No solid–solid phase transitions were observed over the temperature interval from $T = 268$ K to the corresponding melting points for the other compounds.

The mean experimental values of the heat capacity measurements as a function of temperature for solid thiophene and thiane derivatives are given in Tables 4 and 5, respectively. The coefficients of the fitted quadratic equation in temperature are collected in Table 6. The range studied for each compound is given as the last column of this table.

Table 7 gives experimental heat capacity values at $T = 298.15$ K for both liquid and solid compounds with their uncertainties taken as the standard deviation of the mean.

Previous experimental determinations of heat capacity for thiazole by adiabatic calorimetry are given in the literature [42,43]. The value obtained in these previous studies, $C_{p,\mathrm{m}}$ (298.15 K) = 121.0 J K^{-1} mol^{-1} with an estimated error of about 0.2%, are in agreement with the value obtained in this work. To our knowledge, there are no previous experimental results for the rest of the substances.

For comparison purposes and due to the paucity of the experimental data available, some estimated values using the group contribution approach of Chickos et al. [21] with the refined values for cyclic sulfide and cyclic sulfone for solid compounds reported in reference [6], and Zábranský and Růžička [25] are also included in Table 7. Since the estimation method of Zábranský and Růžička has no contributions for the groups C_B-(C_B)(CO)(S), C_B-(N)(S), C_B-(C_B)(C)(S) and C-(C_B)$(H)_2$(CO), the contributions for the groups C_B-$(C_B)_2$(CO), C_B-(H), C_B-(C) and C-(H_2)(C)(C_B), respectively, were used instead. This replacement could lead to a worsening in the agreement of the estimated values with the experimental ones. As noted previously, although a second order group contribution method gives more accurate values, some groups are missing for this approach. A difference between the procedures is the treatment of the carbons in aromatic heterocycles. In the scheme proposed by Růžička and coworkers [20,25], all carbon atoms are considered as aromatic (C_B) independent of the heterocycle, whereas in the approach developed by Chickos et al. [21], the carbons in thiophene are treated as cyclic sp^2 carbons. Benzenoid carbons in the later estimation are carbons on aromatic systems containing six-membered rings and the corresponding heterocyclic derivatives.

Although differences are sometimes higher than the uncertainty of our values, agreement among data obtained using the

Table 6
Coefficients of the fitted curves

Compound	A ($\mathrm{J\,K^{-3}\,mol^{-1}}$)	B ($\mathrm{J\,K^{-2}\,mol^{-1}}$)	C ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	R^2	Interval (K)
2,2’-Bithiophene	0.00563	−2.44763	429.35700	0.998	263–291
3-Acethylthiophene	0.00275	−1.15988	247.96395	0.997	268–302
2-Thiopheneacetic acid	0.00172	−0.53858	167.21488	0.995	268–328
3-Thiopheneacetic acid	0.00275	−1.02992	230.40584	0.999	268–343
2,5-Thiophene-dicarboxylic acid	0.00107	−0.37039	182.23279	0.999	277–445
1,4-Dithiane sulfone	0.00135	−0.45361	167.58079	0.998	270–454
1,3-Oxathiane sulfone	0.00312	−1.23256	238.91319	0.997	268–335
1,4-Oxathiane sulfone	0.00069	0.02996	76.89293	0.999	268–390

Table 7
Experimental and estimated $C_{p,\mathrm{m}}$ (298.15 K) for all the compounds studied

Compound	State	$C_{p,\mathrm{m}}$ (298.15 K), experimental[a] ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	$C_{p,\mathrm{m}}$ (298.15 K), estimated[b] ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	$C_{p,\mathrm{m}}$ (298.15 K), estimated[c] ($\mathrm{J\,K^{-1}\,mol^{-1}}$)
2,2’-Bithiophene	cr	205.5 ± 1.3	141.3	
2-Acetylthiophene	l	205.7 ± 1.5	206.8	199.9
3-Acetylthiophene	cr	146.1 ± 0.8	135.2	
2-Thiopheneacetic acid	cr	159.2 ± 1.0	150.6	
3-Thiopheneacetic acid	cr	168.4 ± 1.0	150.6	
2,5-Thiophenedicarboxylic acid	cr	167.1 ± 2.9	165.6	
Methyl, 2-thiopheneacetate	l	249.8 ± 0.6	250.4	246.4
Methyl, 3-thiopheneacetate	l	250.6 ± 1.7	250.4	246.4
Thiazole	l	122.1 ± 0.7	120.9	124.2
1,4-Dithiane sulfone	cr	152.7 ± 0.9	155.3	
1,3-Oxathiane sulfone	cr	148.1 ± 2.6	146.8	
1,4-Oxathiane sulfone	cr	147.9 ± 1.2	146.8	

[a] This work.
[b] Estimated by the group contribution scheme of reference [21] using the cyclic sufide and cyclic sulfone values from reference [6].
[c] Estimated by the group contribution scheme of reference [25].

different additivity schemes [21,25] and the experimental values are generally good. Despite the simplicity of the first order group contribution method derived by Chickos et al. [21], it proves to be quite reliable and accurate. The biggest difference between the experimental and estimated values was for 2,2’-bithiophene. The melting point of this compound, 304.2 K, is close to 298.15 K and the experimental heat capacity measured at $T = 298.15$ K could be influenced by a premelting process that causes a higher value than the estimated one. In the case of liquid compounds, the agreement is better than in solids. Despite the fact that the refined cyclic sulfone group parameter is only based in two experimental values [6], it provides accurate heat capacities for the sulfones studied in this work.

Correlation of the experimental heat capacity values at 298.15 K versus estimated ones shows the values are distributed randomly on both sides of the line. 2,2’-Bithiophene was not included in the correlation. Eq. (1) was fit to the results for the values estimated using the routine developed by Chickos et al.

$$\begin{aligned} C_{p,\mathrm{m}}&(298.15\,\mathrm{K},\ \text{estimated})\\ &= (1.038 \pm 0.047)\,C_{p,\mathrm{m}}(298.15\,\mathrm{K},\ \text{exptl.})\\ &\quad -(10.08 \pm 8.45);\ R^2 = 0.991 \qquad (1)\end{aligned}$$

The slope of the line is close to 1 showing the reliability of the estimation procedure. However, the intercept is significatively different from zero providing systematically lower estimated values than experimental ones. Additional corrections and refinements should be made to improve the estimation method.

Acknowledgements

We acknowledge the Spanish MCyT/DGI under project BQ2003-05827. M.T. thanks MEC/SEUI, AP2002-0603, Spain for financial support. We are also grateful to Conacyt (México) for financial support via grant No. 45157.

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