J Therm Anal Calorim (2012) 109:441–446
DOI 10.1007/s10973-011-1670-y

Determination of specific heat capacity and standard molar combustion enthalpy of taurine by DSC

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Received: 20 December 2010 / Accepted: 17 May 2011 / Published online: 3 June 2011

Abstract Using XRY-1C calorimeter, the standard molar enthalpy of taurine was determined to be -2546.2 kJ mol^{-1}. The reliability of the instrument used was tested by using naphthalene as reference material; and through comparing the molar combustion enthalpy of naphthalene measured with its standard value found in literature, the absolute error and relative error were found to be 4.53 kJ mol^{-1} and 0.09%, respectively. The melting point and melting enthalpy of taurine were determined by Differential Scanning Calorimetry (DSC), which was found to be 588.45 K and -22.197 kJ mol^{-1}, respectively. Moreover, using the DSC method, the specific heat capacities C_p of taurine was measured and the relationship between C_p and temperature was established. The thermodynamic basic data obtained are available for the exploiting new synthesis method, engineering design and industry production of taurine.

Keywords Taurine · Specific heat capacity · Differential scanning calorimetric · Standard molar enthalpy of combustion

List of symbols

c	The mean specific heat of calorimeter
C	Heat capacity, J g^{-1} K^{-1} or J mol^{-1} K^{-1}
DSC	DSC signal for sample curve at temperature, mV
H	Enthalpy, J mol^{-1} or kJ mol^{-1}
m	Mass of sample, mg
M	Relative molecular mass of substance, or an amount of sample
n	Mole number
Q	Quantity of heat, J mol^{-1} or kJ mol^{-1}
R	The universal gas constant, 8.314 J mol^{-1} K^{-1}
t	Time, min
T	Kelvin temperature, K
U	Internal energy, J mol^{-1} or kJ·mol^{-1}
w	Mass fraction, or mass number

Greek symbols

φ	DSC output signal
Δ	Variable quantity

Superscript

θ	Standard state

Subscripts

bl	Baseline
c	Combustion heat
f	Reaction heat
m	Material, or melting enthalpy
p	Constant pressure
s	Sample
std	Standard sample
v	Constant volume
0	Zero line of DSC

Introduction

Taurine (2-aminothanesulfonic acid, CASRE 107-35-7) is an essential sulfur-containing non-protein amino acid. It is one of the most abundant of the low molecular weight organic constituents in brain and heart for many animals including mammals, and an essential nutrient in the growth of newborns and infants. A variety of physiological functions, pharmacological actions, and pathological conditions

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seem to be regulated by taurine [1, 2]. Using laser monitoring technique, the solubility data of taurine in water and aqueous solution of methanol, ethanol, and 2-propanol were discussed in the temperature range from 274.0 to 353.0 K at our laboratory in advance [2]. To result the facing difficulties and severe challenge and provide an effective method for isolating taurine from the mixture of impurities, it is necessary to supply the thermodynamics basis data of taurine. Therefore, in this manuscript we examined these thermodynamics data of taurine such as the melting point and molar melting enthalpy of taurine were determined by Differential Scanning Calorimetry (DSC), the relation between the specific heat capacity and temperature was discussed, and the constant-volume combustion energies of the pure substance were determined by a precision oxygen bomb calorimeter. Then the standard molar enthalpies of combustion and formation were calculated by thermodynamics principle. So the related studies can provide a thermodynamic basis for taurine further application, and it will plays an important role in gaining high-yield purification of taurine and be available for the exploiting new synthesis method, engineering design and industry production of taurine.

Experiment section

Materials and experiment apparatus

Benzoic acid used in the experiment was of AR grade with mass fraction purity of over 99.5% and was purchased from Shanghai chemical reagent company, R. P. China. Taurine (mass fraction purity of 99.5%) was purchased from Zhengzhou Friend Living Creature Engineering Co. Ltd., China. α - Al_2O_3 is the powder for DSC standard material, provided by the Shimadzu company in Japan.

XRY-1C calorimeter is provided by Changji Geological Instrument Co., Ltd., *Shanghai* in China. DSC-60 Differential Scanning Calorimetry and DTG-60 thermogravimetric-differential scanning calorimetry are provided by the Shimadzu company in Japan. The precision of electronic balance (FA1004, Shanghai Precision &Scientific Instrument Co., Ltd) and microthermometer is, respectively, 0.1 mg and ±0.01 °C. SPN-500 nitrogen generator (the HP analysis technology research institute in Beijing, China.) provides nitrogen atmosphere for the experiment of thermal analysis.

Determination of specific heat capacity

Principle and procedure

To determine the specific heat capacity of taurine by DSC, heat flow signal from the sample is compared to the DSC signal of a calibration standard substance of specific heat known [3–8]. Both curves are corrected by a zero line or base line of correction experiment. Whereby crucibles of both an empty reference and empty sample are separately placed in the furnace, and the system signal drift is measured under identical experimental conditions.

The specific heat capacity of sample determined is accomplished according to a three step technique process at a linear heating rate by DSC-60: (i) assumes that identical instrument settings and conditions are used for each experimental step. (ii) the same empty reference crucible is used for all steps and not removed from the DSC furnace. (iii) The three main steps defined as follows are done by DSC.

Step 1: empty sample crucible is scanned to obtain DSC sign of zero line determined.

Step 2: to scan sample crucible where contains zinc and indium used as the substance of calibration standard.

Step 3: to scan sample crucible in which contains the sample measured.

The experiments were done for each of them at least three times. Specific heat capacity C_p of the substance in Eq. 1 is then calculated as follows:

$$C_{p,\text{sample}} = \frac{M_{\text{standard}}}{M_{\text{sample}}} \times \frac{\varphi_{\text{sample}}(T) - \varphi_0(T)}{\phi_{\text{standard}}(T) - \phi_0(T)} \times C_{p,\text{standard}} \tag{1}$$

where C_p, M, and φ are, respectively, specific heat capacity, mass of sample, and DSC output signal as heat flow rate of some substances, subscript symbols, such as sample, standard and 0 are, respectively, sample measured, standard chemical substance (e.g., zinc, indium), and zero line.

A small amount of powdery solid sample (3–5 mg) was taken and sealed in an aluminum pan of DSC-60 for the analysis. The measurements were made under fixed conditions of which was the constant heating rate of 5 °C min^{-1} and under nitrogen atmosphere (40 mL min^{-1}). α-Al_2O_3 (standard material, Japan Shimadzu Co.) was used as reference sample in the process of analysis. Before the samples were analyzed, the DSC-60 was calibrated with indium (purity = 99.99%, $T_m = 429.78$ K, $\Delta_m H = 28.45$ J g^{-1}) and zincum (purity = 99.99%, $T_m = 419.58$ K, $\Delta_m H = 100.50$ J g^{-1}) (Japan Shimadzu Co.). Data acquisition and online processing were done with TA-60WS Collection Monitor software.

Determination of standard molar combustion enthalpy

Principle and procedure

According to the principle of thermodynamics, when the material is completely burned, the relationship of the constant volume combustion enthalpy $Q_v = \Delta U$ and the constant pressure combustion enthalpy $Q_\mathrm{p} = \Delta H$ was obtained, and represented by Eq. 2,

$$\Delta \mathrm{H} = Q_\mathrm{p} = \Delta U + \Delta n \mathrm{R} T \quad (2)$$

where Δn, R, and T are, respectively, molar variation between the gaseous reactants and products before and after the reaction, the universal gas constant and kelvin temperature of the reaction [9, 10].

When the sample is completely burned, the exothermic heat can make the temperature of calorimeter (bomb) itself and surrounding medium which is water here increased. We can obtain the constant volume combustion enthalpy by measuring the variation of temperature in burning process. The temperature variation (ΔT) is determined by experiment. The combustion reaction heat Q_v can be obtained for the material at constant volume by Eq. 3 after the specific heat of Oxygen Bomb Calorimeter (c) is defined.

$$mQ_\mathrm{v} = (3200C_\mathrm{water} + c)\Delta T + Q_\mathrm{f} \quad (3)$$

where m, C_water, c, Q_f and Q_v are, respectively, mass of sample, the specific heat capacity of the water ($C_\mathrm{water} = 4.18$ J g^{-1} K^{-1}), the heat capacity of calorimeter, additional heat by air in the boom, and the constant-volume combustion energy of the pure substance.

The heat capacity of the Oxygen Bomb Calorimeter can be obtained by the combustion enthalpy of benzoic acid which is used as the standard substance, and $Q_\mathrm{v} = -26460$ J g^{-1} for benzoic acid in the literature [3, 4]. The detailed procedure is described as following: (i) Weigh the benzoic acid about 1 g, press the powder into tablet, make it touch with the ignition wire in which is tied to the two electrodes, then fill the Oxygen at 0.2–0.3 MPa for 1 min. (ii) Put the oxygen bomb into the bottle which filled with water of 3,200 mL. After temperature is constant, the blender is turn on. The metal wire is ignited after 5 min. (iii) Meanwhile, it is that the sample starts combustion when temperature quickly raised. Temperature readings are taken at 5 s intervals before and after the ignition. After temperature reach at the most height point and continue 10 min, the test could be stopped automatically. The principle and procedure of determining for the other substances (e.g., taurine) is same to above-mentioned method.

Results and discussions

Melting temperature and the melting enthalpy of taurine

Taurine was weighed in an electron analytical balance, and was measured by DSC [11, 12]. The results were given to be 588.45 K and −22.197 kJ mol^{-1} respectively, in Fig. 1, for the melting temperature and the molar melting enthalpy of taurine. The experimental result of melting temperature has a light difference between the melting temperature determined by DSC and literature's (Lit. 583.15 K) [7]. The thermal decomposition of taurine was also examined by thermogravimetric analysis method. The result of thermal decomposition (in Fig. 2) shows that its heat stability is not good because it is decomposed as soon as melting.

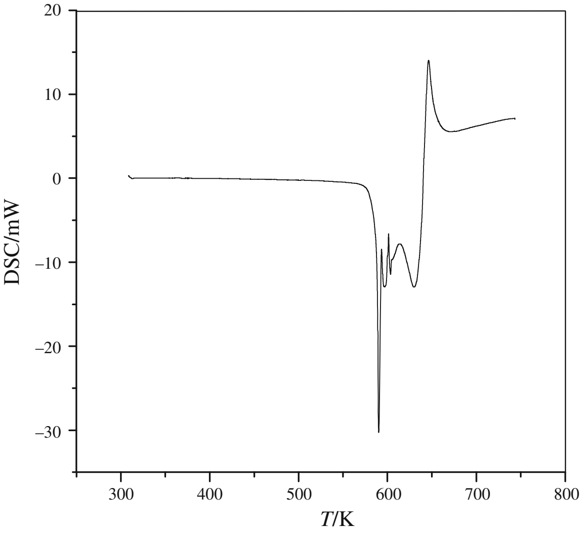

Fig. 1 The heat flow versus temperature of taurine

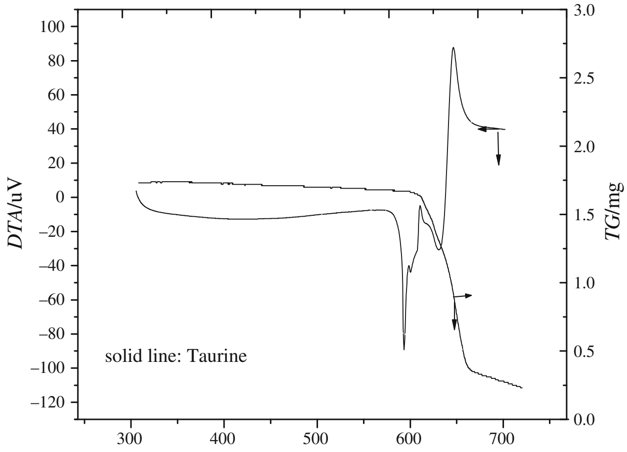

Fig. 2 DTA and TG curves of taurine

Specific heat capacity of taurine

Determination of thermal stability

Several material parameters, such as weight, geometry, and thermal diffusivity, may influence the accuracy of experimental results. One of the most influential factors is baseline stability which will depend largely on the

Table 1 The experimental and literature values of specific heats for α-Al_2O_3

T/K	C_p/kJ kg^{-1} K^{-1} Exptl.	C_p/kJ kg^{-1} K^{-1} Lit.	Error/%
295.15	0.7621	0.7630	0.12
298.15	0.7714	0.7747	0.43
303.15	0.7732	0.7848	0.20
308.15	0.7965	0.7975	0.13
313.15	0.8083	0.8089	0.19
318.15	0.8198	0.8215	0.21
323.15	0.8266	0.8326	0.84
328.15	0.8379	0.8434	0.65
333.15	0.8482	0.8536	0.63
338.15	0.8570	0.9635	0.75
343.15	0.8692	0.8729	0.42
348.15	0.8787	0.8820	0.37
353.15	0.8861	0.8907	0.52
358.15	0.8929	0.8990	0.68
363.15	0.8985	0.9071	0.95
368.15	0.9102	0.9148	0.50
373.15	0.9211	0.9223	0.13

instrument employed. In order to obtain precise measurements, good baseline stability should be guaranteed and needs to be checked at regular intervals. Moreover, the specific heat capacity of α-Al_2O_3 was determined and made it compared to the value of the literature for the sake of determining the reliability of the instrument. The average error between the experimental value and the literature value is less than 1% for α-Al_2O_3 on the base of data in Table 1.

Before the specific heat capacity was measured, temperature and the instrument sensitivity were corrected, respectively, by indium and sapphire as the standard matters. The specific heat capacity of taurine was measured by means of DSC-60 Differential Scanning Calorimeter in the hermetically sealed chamber [13, 14]. The conditions of scanning:reference for α-Al_2O_3, scanned area: 310.15–370.15 K, sample mass is about 5 mg, heating rate is 5 °C min^{-1}. The specific heat capacity was measured at least three times, and the average value is given in Table 2.

Relationship of specific heat capacity at solid phase states and temperature was obtained with the least square method, and represented by Eq. 4,

$$C_p = 0.40487 + 0.00213T(\mathrm{kJ\ kg^{-1}\ K^{-1}}) \tag{4}$$

where the multiple correlation coefficient (R) and the standard deviation (SD) are 0.9897 and 0.00659, respectively. Figure 3 shows the relations between the specific heat specific and temperature for taurine at the solid. Comparing the values calculated by Eq. 4 with the experimental value examined the relative deviation (RD) and average relative deviation (ARD) are listed in Table 2. And average relative deviation is defined as:

Table 2 Experimental results for specific heats of taurine

T/K	C_p/kJ kg^{-1} K^{-1}	$C_{p,cal}$/kJ kg^{-1} K^{-1}	Error/%
310.15	1.0640	1.0655	0.14
315.15	1.0760	1.0761	0.01
320.15	1.0851	1.0868	0.15
325.15	1.0959	1.0974	0.14
330.15	1.1172	1.1081	0.81
335.15	1.1146	1.1187*	0.37
340.15	1.1274	1.1294	0.18
345.15	1.1533	1.1400	1.15
350.15	1.1529	1.1507	0.19
355.15	1.1522	1.1613	0.79
360.15	1.1725	1.1720*	0.04
365.15	1.1784	1.1826	0.40
370.15	1.1979	1.1933	0.38
	RAD		0.36

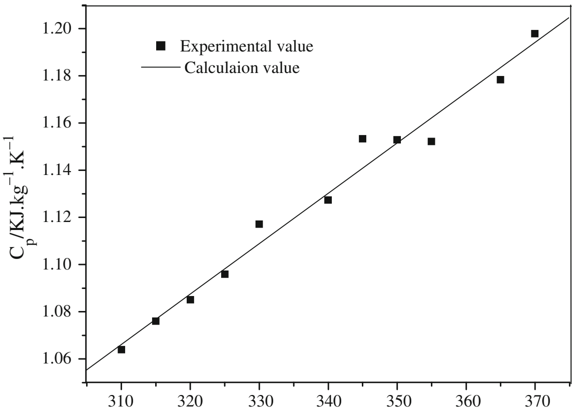

Fig. 3 The specific heat versus temperature curves of taurine at a heating rate of 5 K min^{-1} by DSC

$$\mathrm{ARD} = \frac{1}{n}\sum\left(\frac{\left|C_{p_i} - C_{p_i,\mathrm{cal}}\right|}{C_{pi}}\right) \tag{5}$$

The results show there is good agreement between the experimental and calculated results for the specific heat capacity of taurine. And it also indicates to be believable for them according to RD (to be 0.37 and 0.04, respectively) of two experimental data (at 335.15 and 360.15 K) marked with an asterisk in Table 2 which did not participate in the program regression.

The standard molar combustion enthalpy of taurine

The reliability of the instrument used was tested by using naphthalene as reference material. We compared the molar

Table 3 The energy equivalent of the calorimeter

Compound	$-\Delta_C U^{\theta}_m$/kJ mol^{-1}	$-\Delta_C H^{\theta}_m$/kJ mol^{-1}	$-\Delta_f H^{\theta}_m$/kJ mol^{-1}	m/g	ΔT/°C	c/J K^{-1}	$\bar{c}$/J K^{-1}
Benzoic acid	3228.12[a]	3229.36	382.77	1.0397	1.613	15128	15,221
				0.9955	1.534	15246	
				1.0388	1.667	15289	

[a] Literature value

Table 4 Enthalpy of the standard combustion and formation of samples

Compound	m/g	ΔT/°C	$-\Delta_C U_m$/kJ mol^{-1}	$-\Delta_C H^{\theta}_m$/kJ mol^{-1}	$\Delta_f H^{\theta}_m$/kJ mol^{-1}
Taurine	1.2242	0.874	2554.5	2554.9	470.69
	1.0938	0.743	2430.5	2430.9	346.60
	1.1273	0.787	2497.9	2498.3	414.06
	1.0946	0.826	2700.1	2700.5	616.26
	Average		2545.7	2546.2	461.90
Naphthalene	1.0677	2.819	5156.4	5156.4	
	1.0214	2.694	5157.6	5157.6	
	1.0666	2.812	5161.3	5161.3	
	Average		5158.43	5158.43	

combustion enthalpy of naphthalene measured (-5158.43 kJ mol^{-1}) with its standard value (-5153.9 kJ mol^{-1}) [15] found in the literature. The result indicates that the absolute error and relative error are found to be 4.53 kJ mol^{-1} and 0.09%, respectively.

Freshly planished sample of taurine were used for the combustion in the Oxygen Bomb Calorimeter. Smooth curves were fitted to the pre- and after-period temperatures and the corrected temperature rise was calculated by means of data processing soft-ware in the oxygen bomb calorimeter working station using the Dickinson method, in which ΔT is the ordinate that encloses equal areas above and below the reaction curve. The energy equivalent of the calorimeter c was determined with a standard reference sample of benzoic acid. From four groups of experimental data c was measured to be 15,221 J K^{-1}.

The combustion reaction of taurine can be written as follows:

$$\begin{aligned} C_2H_7O_3NS(s) + \frac{13}{4}O_2(g) \rightarrow 2CO_2(g) + \frac{1}{2}N_2(g) \\ + SO_2(g) + \frac{7}{2}H_2O(l) \end{aligned} \tag{5}$$

After obtaining the Q_v by the Eq. 3, we can get the value of the combustion enthalpy of the taurine. But the combustion enthalpy of taurine is the value at the experiment temperature. On the basis of thermodynamics principle, the standard molar enthalpy of combustion (298.15 K) is

$$\begin{aligned} \Delta_C H^{\theta}_m(298.15\mathrm{K}) &= \Delta H_1 + \Delta_C H_m(T) + \Delta H_2 \\ &= \Delta H_1 + Q_V + \Delta n RT + \Delta H_2 \end{aligned} \tag{6}$$

$$\Delta H_1 = \int_{298.15}^{T} \sum \left(a_j c_{p,j}\right)_{\text{reactant}} dT \tag{7}$$

$$\Delta H_2 = \int_{T}^{298.15} \sum \left(b_k c_{p,k}\right)_{\text{product}} dT \tag{8}$$

which $\Delta_C H^{\theta}_m$ and $\Delta_C H_m$ are the standard molar combustion enthalpy (298.15 K) and the combustion enthalpy at the experiment temperature. ΔH_1 and .ΔH_2. are the enthalpy of the reactants and products. According to the Eq. 6, the individual values of both the standard molar energies and enthalpy of combustion are listed in Table 3 together with the mean.

The standard molar formation enthalpy of taurine

The standard molar enthalpy of formation, $\Delta_f H^{\theta}_m$, was calculated by Hess's law [16] according to the thermochemical Eq. 9 as follow as:

$$\begin{aligned} \Delta_f H^{\theta}_m[C_2H_7O_3NS, s] = \big[2\Delta_f H^{\theta}_m(CO_2, g) \\ +7/2\Delta_f H^{\theta}_m(H_2O, l) + \Delta_f H^{\theta}_m(SO_2, g)\big] \\ - \Delta_C H^{\theta}_m[C_2H_7O_3NS, s] \end{aligned} \tag{9}$$

where

$\Delta_f H^{\theta}_m(CO_2, g) = (-393.509)$kJ mol^{-1},

$\Delta_f H^{\theta}_m(H_2O, l) = (-285.830)$kJ mol^{-1},

$$\Delta_f H_m^\theta(SO_2, g) = (-296.830)\text{kJ mol}^{-1}. \quad (12)$$

The standard molar enthalpy of formation for taurine was calculated to be 461.90 kJ mol^{-1} according to the standard molar enthalpies of combustion (Table 4).

Conclusions

Using XRY-1C calorimeter, the standard molar enthalpy of combustion and formation for taurine was determined to be −2546.2 and 461.90 kJ mol^{-1}. Using DSC differential scanning calorimetric, the thermodynamic basic data such as the melting point, melting enthalpies of taurine, and specific heat capacity, were examined. Relationship between the specific heat capacity of taurine and temperature was accomplished with DSC. So these thermodynamic basic data are available for the exploiting new synthesis method, engineering design and industry production of taurine.

Acknowledgements The authors are pleased to acknowledge financial support from The Zhengzhou's Science and Technology Board, Henan Province, China (0910SGYG23256-6).

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